ELECTROCHEMISTRY

Chapter 17

Chemistry 223
Professor Michael Russell

MAR Last update: 4/29/24

TRANSFER REACTIONS

Atom / Group transfer

$HOAc(aq) + H_2O(l) \rightarrow OAc^{-1}(aq) + H_3O^+(aq)$

Electron transfer

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

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TRANSFER REACTIONS

Electron Transfer Reactions:

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

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

and

$2 Ag^+(aq) + 2 e^- \rightarrow 2 Ag(s)$

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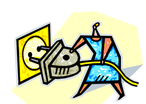
Electron Transfer Reactions

Electron transfer reactions are oxidation-reduction or redox reactions.

Redox reactions can result in the generation of an electric current or be caused by imposing an electric current.

Therefore, this field of chemistry is often called ELECTROCHEMISTRY.



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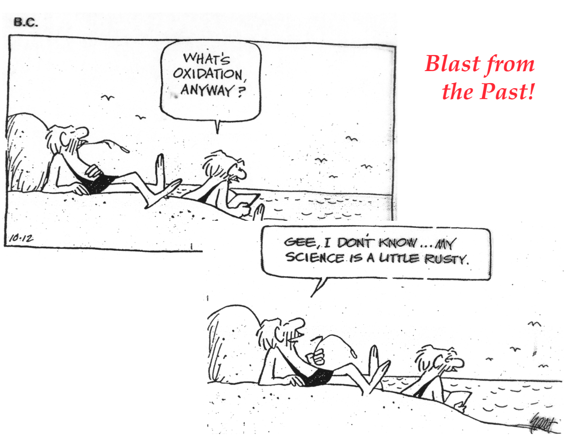

Blast from the Past!

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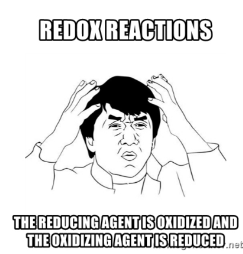
OXIDATION - loss of electron(s) by a species; increase in oxidation number.

REDUCTION - gain of electron(s); decrease in oxidation number.

OXIDIZING AGENT - electron acceptor; species is reduced.

REDUCING AGENT - electron donor; species is oxidized.

Review of Terminology for Redox Reactions



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LEO says GER

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LEO says GER

Lose **E**lectrons **O**xidized

Gain **E**lectrons **R**educed

$Zn(s) \rightarrow Zn^{2+} + 2e^-$ ***Oxidized***

$Cu^{2+} + 2e^- \rightarrow Cu(s)$ ***Reduced***

*Can also use **"OIL RIG"**:*
OIL = "Oxidation is Losing" *(electrons)*
RIG = "Reduction is Gaining" *(electrons)*

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OXIDATION-REDUCTION REACTIONS

Direct Redox Reaction

Oxidizing and reducing agents in direct contact.

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

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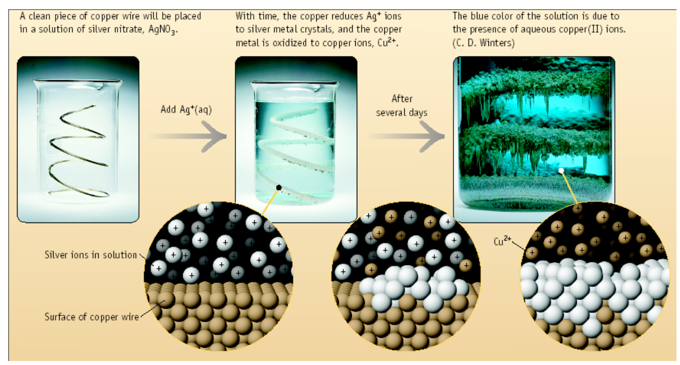
Copper + Silver Ion



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OXIDATION-REDUCTION REACTIONS

Indirect Redox Reaction

A battery functions by transferring electrons through an external wire from the reducing agent to the oxidizing agent.

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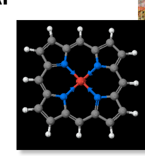
Why Study Electrochemistry?

- **Batteries**
- **Corrosion**
- **Industrial production of chemicals such as Cl_2, NaOH, F_2 and Al**
- **Biological redox reactions**

A rusted car



The heme group

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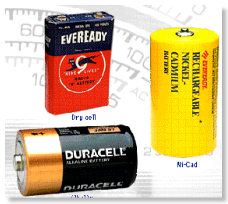
Electrochemical Cells

An apparatus that allows a redox reaction to occur by transferring electrons through an external connector.

Product favored reaction ---> voltaic or galvanic cell ----> electric current created

Reactant favored reaction ---> electrolytic cell ---> electric current used to cause chemical change



Batteries are voltaic cells

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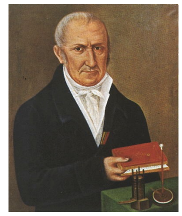
Famous Electrochemists



Alessandro Volta, 1745-1827, Italian scientist and inventor.

Luigi Galvani, 1737-1798, Italian scientist and inventor.

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Balancing Equations for Redox Reactions

Some redox reactions have equations that must be balanced by special techniques.

MnO_4^- + 5 Fe^{2+} + 8 H^+
Mn = +7   Fe = +2

$\rightarrow$ Mn^{2+} + 5 Fe^{3+} + 4 H_2O
Mn = +2   Fe = +3

See: Redox Reactions Handout

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Balancing Equations

Consider the reduction of Ag^+ ions with copper metal.

Cu + Ag^+ --gives--> Cu^{2+} + Ag

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Balancing Equations

Step 1: Divide the reaction into half-reactions, one for oxidation and the other for reduction.

Ox Cu $\rightarrow$ Cu^{2+}

Red Ag^+ $\rightarrow$ Ag

Step 2: Balance each for mass. Already done in this case.

Step 3: Balance each half-reaction for charge by adding electrons.

Ox Cu $\rightarrow$ Cu^{2+} + 2e-

Red Ag^+ + e- $\rightarrow$ Ag

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Balancing Equations

Step 4: Multiply each half-reaction by a factor that means the reducing agent supplies as many electrons as the oxidizing agent requires.

Reducing agent $Cu \rightarrow Cu^{2+} + 2e^-$

Oxidizing agent $2\ Ag^+ + 2\ e^- \rightarrow 2\ Ag$

Step 5: Add half-reactions to give the overall equation.

$$Cu + 2\ Ag^+ \rightarrow Cu^{2+} + 2\ Ag$$

The equation is now balanced for both charge and mass.

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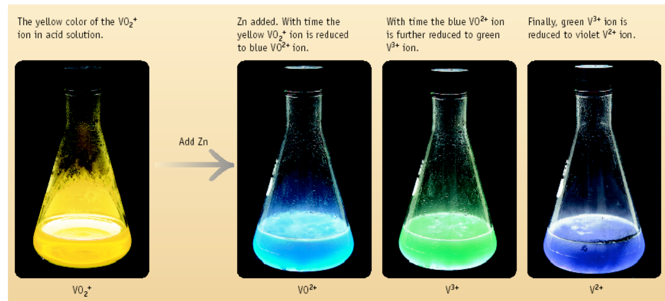
Reduction of VO_2^+ with Zn



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Balancing Equations

Balance the following in *acidic* solution-

$VO_2^+ + Zn \rightarrow VO^{2+} + Zn^{2+}$

Step 1: Write the half-reactions

Ox $Zn \rightarrow Zn^{2+}$

Red $VO_2^+ \rightarrow VO^{2+}$ *($V^{5+} \rightarrow V^{4+}$)*

Step 2: Balance each half-reaction for mass.

Ox $Zn \rightarrow Zn^{2+}$

Red $VO_2^+ \rightarrow VO^{2+} + H_2O$

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Balancing Equations

Balance the following in *acidic* solution-

$VO_2^+ + Zn \rightarrow VO^{2+} + Zn^{2+}$

Step 1: Write the half-reactions

Ox $Zn \rightarrow Zn^{2+}$

Red $VO_2^+ \rightarrow VO^{2+}$ *(V^{5+} --> V^{4+})*

Step 2: Balance each half-reaction for mass.

Ox $Zn \rightarrow Zn^{2+}$

Red $2\ H^+ + VO_2^+ \rightarrow VO^{2+} + H_2O$

Add H_2O on O-deficient side and add H^+ on other side for balancing hydrogen

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Balancing Equations

Step 3: Balance half-reactions for charge.

Ox $Zn \rightarrow Zn^{2+} + 2e^-$

Red $e^- + 2\ H^+ + VO_2^+ \rightarrow VO^{2+} + H_2O$

Step 4: Multiply by an appropriate factor.

Ox $Zn \rightarrow Zn^{2+} + 2e^-$

Red $2\ e^- + 4\ H^+ + 2\ VO_2^+ \rightarrow 2\ VO^{2+} + 2\ H_2O$

Step 5: Add half-reactions

$$Zn + 4\ H^+ + 2\ VO_2^+ \rightarrow Zn^{2+} + 2\ VO^{2+} + 2\ H_2O$$

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Balancing Equations

Balance the following in *basic* solution-

$MnO_4^{1-} + HO_2^- \rightarrow MnO_4^{2-} + O_2$

Step 1: Write the half-reactions

Ox $HO_2^- \rightarrow O_2$ *(peroxide: $O^{-1} \rightarrow O^0$)*

Red $MnO_4^{1-} \rightarrow MnO_4^{2-}$ *($Mn^{7+} \rightarrow Mn^{6+}$)*

Step 2: Balance each half-reaction for mass.

Red $MnO_4^{1-} \rightarrow MnO_4^{2-}$

Ox $HO_2^- \rightarrow O_2 + H_2O$

MnO_4^{-1} = permanganate
MnO_4^{2-} = manganate

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Balancing Equations

Balance the following in *basic* solution-

$MnO_4^{1-} + HO_2^- \rightarrow MnO_4^{2-} + O_2$

Step 1: Write the half-reactions

Ox $HO_2^- \rightarrow O_2$ *(peroxide: $O^{-1} \rightarrow O^0$)*

Red $MnO_4^{1-} \rightarrow MnO_4^{2-}$ *($Mn^{7+} \rightarrow Mn^{6+}$)*

Step 2: Balance each half-reaction for mass.

Red $MnO_4^{1-} \rightarrow MnO_4^{2-}$

Ox $OH^- + HO_2^- \rightarrow O_2 + H_2O$

Add H_2O on H-deficient side and add OH^- on other side for balancing oxygen

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Balancing Equations

Step 3: Balance half-reactions for charge.

Ox $OH^- + HO_2^- \rightarrow O_2 + H_2O + 2e-$

Red $e- + MnO_4^{1-} \rightarrow MnO_4^{2-}$

Step 4: Multiply by an appropriate factor.

Ox $OH^- + HO_2^- \rightarrow O_2 + H_2O + 2e-$

Red $2\ e- + 2\ MnO_4^{1-} \rightarrow 2\ MnO_4^{2-}$

Step 5: Add half-reactions

$OH^- + HO_2^- + 2\ MnO_4^{1-} \rightarrow O_2 + H_2O + 2\ MnO_4^{2-}$

*Add H_2O on H-deficient side and add OH^- on other side for balancing oxygen **in basic solution***

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Alternate Basic Balancing Method

Balance basic reactions first with acid, then "neutralize" with OH^-. *Previous example:*

$MnO_4^{1-} + HO_2^- \rightarrow MnO_4^{2-} + O_2$

Step 1: Write the half-reactions

Ox $HO_2^- \rightarrow O_2$

Red $MnO_4^{1-} \rightarrow MnO_4^{2-}$

Step 2: Balance each half-reaction for mass - use H^+ and/or H_2O.

Red $MnO_4^{1-} \rightarrow MnO_4^{2-}$

Ox $HO_2^- \rightarrow O_2 + H^+$

Add H^+ to H-deficient side and H_2O to balance oxygen

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Alternate Basic Balancing Method

Step 3: Balance half-reactions for charge.

Ox $HO_2^- \rightarrow O_2 + H^+ + 2e-$

Red $e- + MnO_4^{1-} \rightarrow MnO_4^{2-}$

Step 4: Multiply by an appropriate factor.

Ox $HO_2^- \rightarrow O_2 + H^+ + 2e-$

Red $2\ e- + 2\ MnO_4^{1-} \rightarrow 2\ MnO_4^{2-}$

Step 5: Add half-reactions

$HO_2^- + 2\ MnO_4^{1-} \rightarrow O_2 + H^+ + 2\ MnO_4^{2-}$

This equation is balanced for pH < 7 but not base

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Alternate Basic Balancing Method

Step 6: Neutralize H^+ by adding OH^-.
H^+ and OH^- make H_2O.
Add OH^- to *both* sides of equation

$HO_2^- + 2\ MnO_4^{1-} + OH^- \rightarrow O_2 + H^+ + OH^- + 2\ MnO_4^{2-}$

$HO_2^- + 2\ MnO_4^{1-} + OH^- \rightarrow O_2 + H_2O + 2\ MnO_4^{2-}$

Use either method to balance basic redox reactions

Also see the Redox Reactions Handout

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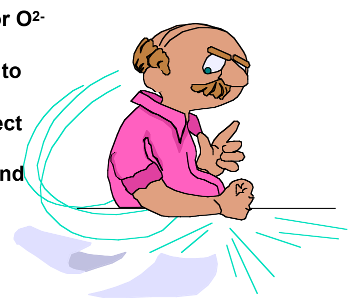
Tips on Balancing Equations

- Determine the pH of the reaction.
- Never add O_2, O atoms, or O^{2-} to balance oxygen.
- Never add H_2 or H atoms to balance hydrogen.
- Be sure to write the correct charges on all the ions.
- Check your work at the end to make sure mass and charge are balanced.
- *See: Redox Reactions Handout*



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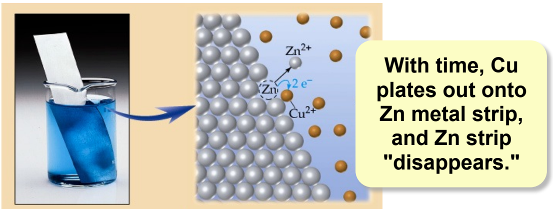
CHEMICAL CHANGE --> ELECTRIC CURRENT



Zn is oxidized and is the reducing agent

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

Cu^{2+} is reduced and is the oxidizing agent

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

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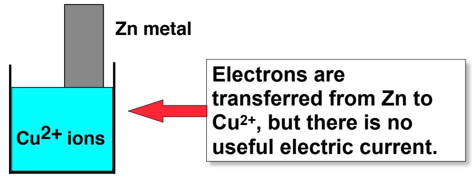
CHEMICAL CHANGE --> ELECTRIC CURRENT



Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

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

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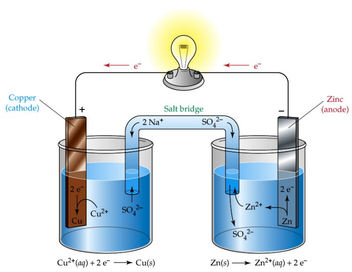
CHEMICAL CHANGE --> ELECTRIC CURRENT

To obtain a useful current, we separate the oxidizing and reducing agents so that electron transfer occurs through an external wire.

This is accomplished in a GALVANIC or VOLTAIC cell.

A group of such cells is called a battery.



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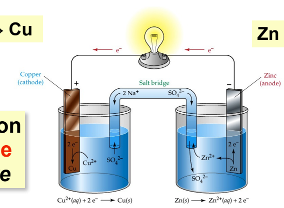
$Cu^{2+} + 2e^- \rightarrow Cu$

$Zn \rightarrow Zn^{2+} + 2e^-$

Reduction
Cathode
Positive



Oxidation
Anode
Negative

Anions-->
<--Cations

Electrons travel through external wire. Salt bridge allows anions and cations to move between electrode compartments, maintaining electrical neutrality.

Salt Bridge

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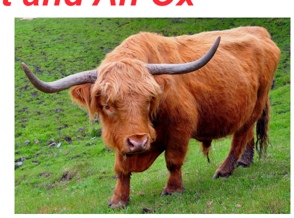
Red Cat = REDuction
at the CAThode
$Cu^{2+} + 2e^- \rightarrow Cu$

A Red Cat and An Ox



An Ox = OXidation
at the ANode
$Zn \rightarrow Zn^{2+} + 2e^-$

also remember:
oxidation = reducing agent
reduction = oxidizing agent

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SHORTHAND NOTATION for GALVANIC CELLS

$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$
can also be written as:

anode half cell — *cathode half cell*

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

phase boundary — *salt bridge* — *phase boundary*

Electrons flow this way →

oxidation — *reduction*

FAT CAT = *electrons flow* **F**rom **A**node **T**o **CAT**hode

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SHORTHAND NOTATION for GALVANIC CELLS

Example: Describe the following *galvanic* cell:

Cu(s) | Cu^{2+}(1.0 M) || Cl_2(1.0 atm) | Cl^-(1.0 M) | Pt(s)

Solution:

The **anode** (oxidation) is: **$Cu(s) \rightarrow Cu^{2+}_{(aq)} + 2\ e^-$**
and $[Cu^{2+}]$ = 1.0 M

The **cathode** (reduction) is: **$Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-_{(aq)}$**
and $[Cl^-]$ = 1.0 M and $P(Cl_2)$ = 1.0 atm

The cathode uses a **Platinum electrode** to transfer electrons to the $Cl_{2(g)}$. The Pt does not react chemically with the electrons

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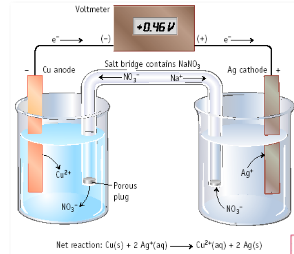
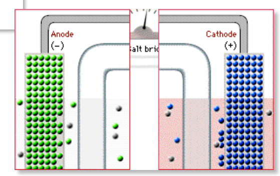


Electrons move from anode to cathode in the wire. Anions (*mostly*) move through the salt bridge.



Cu I Cu^{2+} II Ag^+ I Ag

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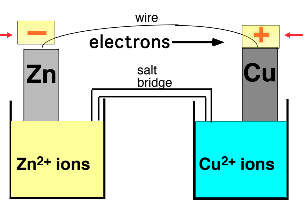
Sign of Battery Terminals (Galvanic Cells Only)

Anode, site of ***oxidation***, **negative**



Cathode, site of ***reduction***, **positive**

Electrons flow away from the "negative" terminal (anode) and to the "positive" terminal (cathode) in Galvanic cells

Electrolytic cells use opposite signs

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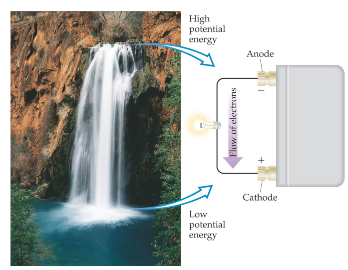
Electromotive Force (emf)



Water only spontaneously flows one way in a waterfall.

Likewise, electrons only spontaneously flow one way in a redox reaction—from higher to lower potential energy.

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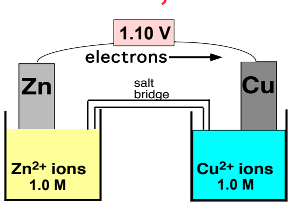
CELL POTENTIAL, E



Electrons are "driven" from anode to cathode by an electromotive force or emf.

For Zn/Cu cell, this is indicated by a voltage of 1.10 V at 25 ˚C and when $[Zn^{2+}]$ and $[Cu^{2+}]$ = 1.0 M.

Note that 1 V = 1 J/C, more on this later

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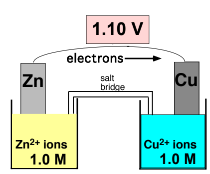

CELL POTENTIAL, E

For Zn/Cu cell, voltage is 1.10 V at 25 ˚C and when $[Zn^{2+}]$ and $[Cu^{2+}]$ = 1.0 M.

This is the *STANDARD* CELL POTENTIAL, E˚

E˚ *(measured in* Volts, V*)* is a quantitative measure of the tendency for reactants to proceed to products when all are in their standard states at 1.0 M and 25 ˚C.

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Calculating Cell Voltage

Balanced half-reactions can be added together to get overall, balanced equation.

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

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

If we know E° for each half-reaction, we can calculate E° for net reaction.

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CELL POTENTIALS, E°

Cannot measure 1/2 reaction E° directly. Therefore, measure it relative to a STANDARD HYDROGEN CELL, SHE.

(SHE = Standard Hydrogen Electrode)

$2 H^+(aq, 1 M) + 2e- \rightleftarrows H_2(g, 1 atm)$

E° = 0.00 V

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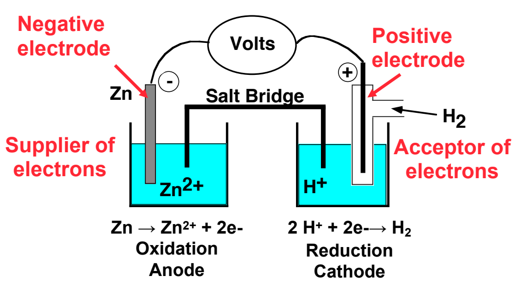
Zn/SHE half cell



E° for the cell = +0.76 V (measured)

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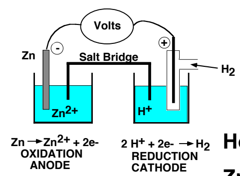
Zn/SHE half cell



How to find the zinc half cell potential, $E_{Zn}°$:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e-$ — $E_{Zn}° = ?$
$2 H^+(aq) + 2e- \rightarrow H_2(g)$ — $E_{H+}° = 0.00$ V

$Zn(s) + 2 H^+(aq) \rightarrow Zn^{2+} + H_2(g)$ — $E_{net}° = +0.76$ V

so $E_{zn}° = E_{net}° - E_{H+}° = 0.76 - 0.00 = +0.76$ V

Therefore, E° for $Zn \rightarrow Zn^{2+}(aq) + 2e-$ is +0.76 V

Zn is a better reducing agent than H_2.

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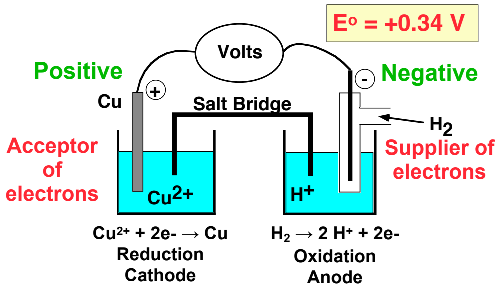
Cu/Cu^{2+} and H_2/H^+ Cell

E° = +0.34 V



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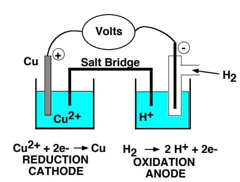
Cu/Cu^{2+} and H_2/H^+ Cell



Overall reaction is reduction of Cu^{2+} by H_2 gas.

$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2 H^+(aq)$

Measured E° = +0.34 V

Therefore, E° for $Cu^{2+} + 2e- \rightarrow Cu$ is

+0.34 V

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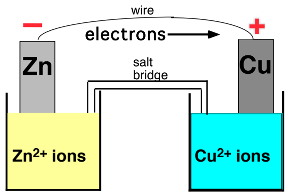
Zn/Cu Electrochemical Cell

Anode, negative, source of electrons



Cathode, positive, sink for electrons

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ E° = +0.76 V

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ E° = +0.34 V

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

E° (calc'd) = +1.10 V

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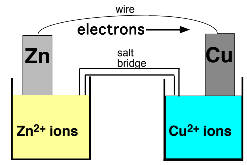
Uses of E° Values

Half-reactions organized by relative ability to act as *oxidizing agents*

Use tables of reduction potentials in your textbook or problem set to predict the direction of redox reactions.



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Reversing Half Reactions

Reversing half reactions changes the **sign** ***but not the magnitude*** of E° values

Example:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ E° = +0.76 V

would become

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ E° = -0.76 V

Because E° tables listed as reductions, many negative E° values will appear

Negative E° values imply great oxidizers / reducing agents

Positive E° values imply great reducers / oxidizing agents

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reducing ability increases *or* oxidizing agent capacity increases

Standard Reduction Potentials in Aqueous Solution at 25 °C*

Reduction Half-Reaction		E° (V)
$F_2(g) + 2\ e^-$	$\longrightarrow 2\ F^-(aq)$	+2.87
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^-$	$\longrightarrow 2\ H_2O(\ell)$	+1.77
$PbO_2(s) + SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^-$	$\longrightarrow PbSO_4(s) + 2\ H_2O(\ell)$	+1.685
$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^-$	$\longrightarrow Mn^{2+}(aq) + 4\ H_2O(\ell)$	+1.52
$Au^{3+}(aq) + 3\ e^-$	$\longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2\ e^-$	$\longrightarrow 2\ Cl^-(aq)$	+1.360
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^-$	$\longrightarrow 2\ Cr^{3+}(aq) + 7\ H_2O\ (\ell)$	+1.33
$O_2(g) + 4\ H^+(aq) + 4\ e^-$	$\longrightarrow 2\ H_2O(\ell)$	+1.229
$Br_2(\ell) + 2\ e^-$	$\longrightarrow 2\ Br^-(aq)$	+1.08
$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^-$	$\longrightarrow NO(g) + 2\ H_2O(\ell)$	+0.96
$OCl^-(aq) + H_2O(\ell) + 2\ e^-$	$\longrightarrow Cl^-(aq) + 2\ OH^-(aq)$	+0.89
$Hg^{2+}(aq) + 2\ e^-$	$\longrightarrow Hg(\ell)$	+0.855
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	+0.80
$Hg_2^{2+}(aq) + 2\ e^-$	$\longrightarrow 2\ Hg(\ell)$	+0.789
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	+0.771
$I_2(s) + 2\ e^-$	$\longrightarrow 2\ I^-(aq)$	+0.535
$O_2(g) + 2\ H_2O(\ell) + 4\ e^-$	$\longrightarrow 4\ OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2\ e^-$	$\longrightarrow Cu(s)$	+0.337
$Sn^{4+}(aq) + 2\ e^-$	$\longrightarrow Sn^{2+}(aq)$	+0.15
$2\ H^+(aq) + 2\ e^-$	$\longrightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2\ e^-$	$\longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2\ e^-$	$\longrightarrow Ni(s)$	−0.25
$V^{3+}(aq) + e^-$	$\longrightarrow V^{2+}(aq)$	−0.255
$PbSO_4(s) + 2\ e^-$	$\longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.356
$Cd^{2+}(aq) + 2\ e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2\ e^-$	$\longrightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2\ e^-$	$\longrightarrow Zn(s)$	−0.763
$2\ H_2O(\ell) + 2\ e^-$	$\longrightarrow H_2(g) + 2\ OH^-(aq)$	−0.8277
$Al^{3+}(aq) + 3\ e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2\ e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.714
$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.925
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.045

Increasing strength of oxidizing agents (↑) / Increasing strength of reducing agents (↓)

*In volts (V) versus the standard hydrogen electrode.

oxidizing ability increases *or* reducing agent capacity increases

MAR

Standard Redox Potentials, E°

$Cu^{2+} + 2\ e^- \rightarrow Cu$ +0.34

$2\ H^+ + 2\ e^- \rightarrow H_2$ 0.00

$Zn^{2+} + 2e^- \rightarrow Zn$ -0.76

Any substance on the right will reduce any substance higher than it on the left.

Northwest-southeast rule: product-favored reactions occur between reducing agent at southeast corner (anode) and oxidizing agent at northwest corner (cathode).

MAR

Calculating E° (Michael's Method)

Flip one half-reaction from table (and E° value), then *add* oxidation and reduction values

Example: Determine E° for the following:

$2\ Al + 3\ Ni^{2+} \rightarrow 2\ Al^{3+} + 3\ Ni$

Solution: From redox tables we find:

$Al^{3+} + 3\ e^- \rightarrow Al$ E° = -1.66 V

$Ni^{2+} + 2\ e^- \rightarrow Ni$ E° = -0.25 V

Ni^{2+} ok as written; need to flip Al^{3+} reaction to:

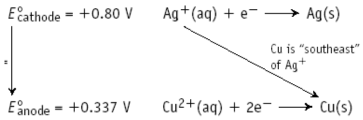
$Al \rightarrow Al^{3+} + 3\ e^-$ E° = +1.66 V

So: E° = 1.66 - 0.25 = 1.41 V

MAR

Calculating E°

Calculate E°_{net} for reaction between Cu and Ag^+ ions



$Ag^+ + e^- \rightarrow Ag$ $E^\circ = 0.80$ V

$Cu^{2+} + 2e^- \rightarrow Cu$ $E^\circ = 0.337$ V

*Ag^+ ok as written; need to **flip** Cu^{2+} reaction to:*

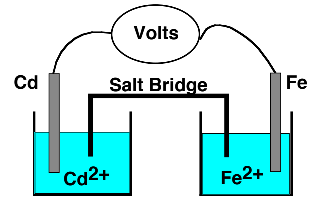
$Cu \rightarrow Cu^{2+} + 2e^-$ $E^\circ = -0.337$ V

E°_{net} *for Cu/Ag+ reaction* = 0.80 - 0.337 = +0.46 V

balanced reaction: $Cu + 2\,Ag^+ \rightarrow 2\,Ag + Cu^{2+}$

MAR

E° for a Voltaic Cell



$Cd \rightarrow Cd^{2+} + 2e^-$ *and* $Fe^{2+} + 2e^- \rightarrow Fe$

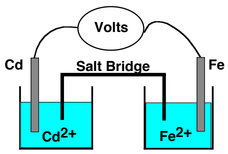
or *or*

$Cd^{2+} + 2e^- \rightarrow Cd$ *and* $Fe \rightarrow Fe^{2+} + 2e^-$

All ingredients are present.
Which way does the reaction proceed?

MAR

E° for a Voltaic Cell



From tables, you see:

$Fe^{2+} + 2e^- \rightarrow Fe$ $E^\circ = -.40$

$Cd^{2+} + 2e^- \rightarrow Cd$ $E^\circ = -.44$

Reaction occurs spontaneously when E° values are positive

Overall reaction:

$Fe^{2+} + Cd \rightarrow Cd^{2+} + Fe$

$E^\circ = E^\circ_{cathode} - E^\circ_{anode}$

$= (-0.40\text{ V}) - (-0.44\text{ V})$

$= +0.04$ V

MAR

More About Calculating Cell Voltage

Can I^- ion reduce water? From tables:

$2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$ $E^\circ = -.828$ V

$2\,I^- \rightarrow I_2 + 2e^-$ $E^\circ = -.535$ V

$2\,I^- + 2\,H_2O \rightarrow I_2 + 2\,OH^- + H_2$

Assuming reaction occurs as written,

$E^\circ_{net} = E^\circ_{red} + E^\circ_{ox} = -0.828\text{ V} - 0.535\text{ V} = -1.363$ V

Minus E° means rxn occurs in opposite direction!

$I_2 + 2OH^- + H_2 \rightarrow 2I^- + 2H_2O$ $E^\circ = +1.363$ V

I^- ion does not reduce water spontaneously!

MAR

More About Calculating Cell Voltage

Can we *make* the I^- ion reduce water?

$2\,I^- + 2\,H_2O \rightarrow I_2 + 2\,OH^- + H_2$ $E^\circ = -1.363$ V

Non-spontaneous (negative E°) reactions can be "forced" to occur with external voltage

Voltage can be applied through battery, other voltaic cells, etc.

Applying 1.363 V to the above electrolytic cell will cause the I^- reduce water - electrolysis

Are we cheating the second law of thermodynamics?

MAR

E° and ΔG°

E° is related to ΔG°, the free energy change for the reaction.

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

where F = Faraday constant
= 9.6485×10^4 C/mol e^-

and n is the number of moles of electrons transferred

Michael Faraday
1791-1867

***Memorize** the value of F!*

Always use 96485 for F!

MAR

E° and ΔG°

$\Delta G° = - n F E°$

For a product-favored reaction

Reactants → Products

ΔG° < 0 and so E° > 0

E° is positive

For a reactant-favored reaction

Reactants ← Products

ΔG° > 0 and so E° < 0

E° is negative

MAR

Quantitative Aspects of Electrochemistry

Consider electrolysis of aqueous silver ion.

Ag^+ (aq) + e- → Ag(s)

1 mol e- → 1 mol Ag

If we could measure the moles of e-, we could know the quantity of Ag formed.

But how to measure moles of e-?

$$\text{Current} = \frac{\text{charge passing}}{\text{time}} \qquad \text{I (amps)} = \frac{\text{coulombs}}{\text{seconds}}$$

MAR

Quantitative Aspects of Electrochemistry

$$\text{Amps} = \frac{\text{coulombs}}{\text{seconds}}$$

A current of 1.50 amps (1.50 C/s) flows through a Ag^+(aq) solution for 15.0 min. What mass of Ag metal is deposited?

Solution

(a) Calculate charge in Coulombs (C)

1.50 amps = 1.50 C/s

= (1.50 C/s)(60 s/min)(15.0 min) = 1350 C

MAR

Quantitative Aspects of Electrochemistry

$$\text{Amps} = \frac{\text{coulombs}}{\text{seconds}}$$

A current of 1.50 amps (1.50 C/s) flows through a Ag^+(aq) solution for 15.0 min. What mass of Ag metal is deposited?

Solution

(a) Charge = 1350 C

(b) Calculate moles of e- used *(F = 96,485 C/mol e-)*

$$1350 \text{ C} \bullet \frac{1 \text{ mol e-}}{96{,}485 \text{ C}} = 0.0140 \text{ mol e-}$$

(c) Calc. quantity of Ag

$$0.0140 \text{ mol e-} \bullet \frac{1 \text{ mol Ag}}{1 \text{ mol e-}} = 0.0140 \text{ mol Ag or } 1.51 \text{ g Ag}$$

MAR

Quantitative Aspects of Electrochemistry

The *anode reaction* in a lead storage battery is

$Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e-$

If a battery delivers 1.50 amp, and you have 454 g of Pb, how long will the battery last?

Solution

a) 454 g Pb = 2.19 mol Pb

b) Calculate moles of e-

$$2.19 \text{ mol Pb} \bullet \frac{2 \text{ mol e-}}{1 \text{ mol Pb}} = 4.38 \text{ mol e-}$$

c) Calculate charge

4.38 mol e- • 96,485 C/mol e- = 423,000 C

MAR

Quantitative Aspects of Electrochemistry

The anode reaction in a lead storage battery is

$Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e-$

If a battery delivers 1.50 amp, and you have 454 g of Pb, how long will the battery last?

Solution

a) 454 g Pb = 2.19 mol Pb

b) Mol of e- = 4.38 mol

c) Charge = 423,000 C

d) Calculate time $\quad \text{Time } (s) = \frac{\text{Charge (C)}}{\text{I (amps)}}$

$$\text{Time } (s) = \frac{423{,}000 \text{ C}}{1.50 \text{ amp}} = 282{,}000 \text{ s}$$

About 78.3 hours

MAR

The Nernst Equation

Q, the reaction quotient, can be related to non standard cell potentials, E

E is related to Q, the reaction quotient, by:

$$E = E° - (RT/nF) \ln Q$$

where R = Gas constant (8.3145 J/K mol)

T = Temperature (K)

F = Faraday constant

E° = standard cell potential

and n = the number of moles of electrons transferred

This is the Nernst Equation (*Handout*)

MAR

The Nernst Equation

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

For Zn/Cu cell, voltage is 1.10 V at 25 ˚C when $[Zn^{2+}]$ and $[Cu^{2+}]$ = 1.0 M

Adding $Cu^{2+}_{(aq)}$ shifts reaction right (Le Chatelier's Principle), making reaction more spontaneous (ΔG) and E° more positive

MAR

The Nernst Equation

Example: Find E when $[Zn^{2+}]$ = 0.0010 M, $P(H_2)$ = 0.10 atm and pH = 0 at 290. K.

Solution: *Find E° for reaction under standard conditions first*

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e-$ E° = 0.76 V

$2 H^+(aq) + 2e- \rightarrow H_2(g)$ E° = 0.00 V

$2 H^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + H_2(g)$

$E°_{net}$ = 0.76 V

Note that n = 2

MAR

The Nernst Equation

Example: Find E when $[Zn^{2+}]$ = 0.0010 M, $P(H_2)$ = 0.10 atm and pH = 0 at 290. K. $[H^+]$ = 1.0 M

$2 H^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + H_2(g)$ $E°_{net}$ = 0.76 V

Solution

Use Nernst Equation:

$E = E° - (RT/nF) \ln Q$

E = 0.76 V - (8.3145 * 290. K / 2 * 96485) ln Q

$[H^+] = 10^{-pH}$ M = 10^{-0} M = 1.0 M

$Q = [Zn^{2+}] * P_{H2} / [H^+]^2 = [0.0010 * 0.10 / (1.0)^2]$

E = 0.76 V + 0.12 V = 0.88 V

MAR

E° and K

At Equilibrium (K), combine ΔG expressions for E° and K to get:

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

If at 298 K, can use:

$$E^\circ = \frac{0.0257}{n} \ln K$$

Only valid at 298 K!

Find equilibrium constants from E˚ data!

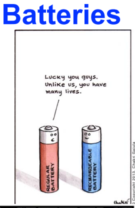
MAR

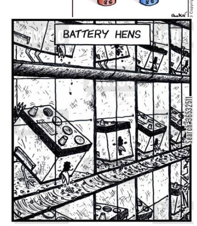
Electrochemical Processes in Batteries

A **battery** consists of self-contained voltaic cells arranged in series, so their individual voltages are added.

A **primary battery** cannot be recharged. The battery is "dead" when the cell reaction has reached equilibrium.

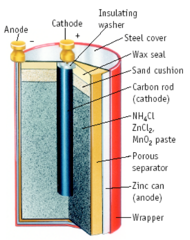
A **secondary battery** is rechargeable. Once it has run down, electrical energy is supplied to reverse the cell reaction and form more reactant.

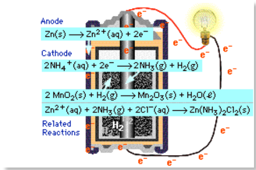




MAR

Dry Cell Battery





A **primary battery** - uses reactions that cannot be recharged

Anode (-)

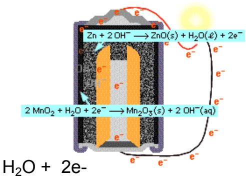
$Zn \rightarrow Zn^{2+} + 2e^-$

Cathode (+)

$2 NH_4^+ + 2e^- \rightarrow 2 NH_3 + H_2$

MAR

Alkaline Battery



Nearly same reactions as in common dry cell, but under basic conditions.

Anode (-): $Zn + 2 OH^-$ ---> $ZnO + H_2O + 2e^-$

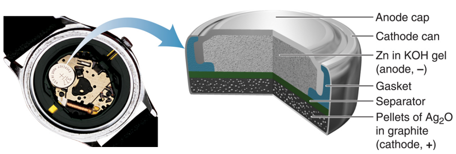
Cathode (+): $2 MnO_2 + H_2O + 2e^-$ ---> $Mn_2O_3 + 2 OH^-$

$Zn(s) + MnO_2(s) + H_2O(l) \rightarrow ZnO(s) + Mn(OH)_2(s)$

$E_{cell} = 1.5$ V

MAR

Silver Button Battery



Anode (oxidation): $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode (reduction): $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$

Overall (cell) reaction: $Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$

$E_{cell} = 1.6$ V

MAR

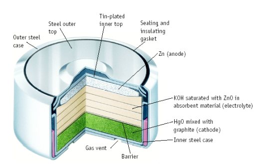
Mercury Button Battery

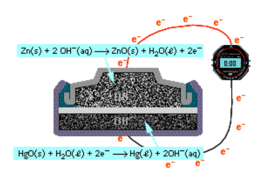
Anode:

Zn is reducing agent under basic conditions

Cathode:

$HgO + H_2O + 2e^- \rightarrow Hg + 2 OH^-$





MAR

Lead-Acid Storage Battery

Anode (0.36 V): $Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$

Cathode (1.68 V):

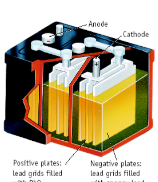
$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

Overall (cell) reaction (discharge):

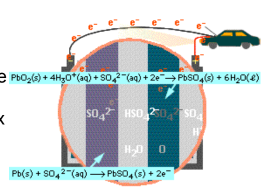
$PbO_2(s) + Pb(s) + H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$ $E_{cell} = 2.04$ V

Overall (cell) reaction (recharge):

$2PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + Pb(s) + H_2SO_4(aq)$



A **secondary battery** - can be recharged, reversible redox reactions



MAR

Nickel-Cadmium Battery

Anode (-):

$Cd + 2 OH^- \rightarrow Cd(OH)_2 + 2e^-$

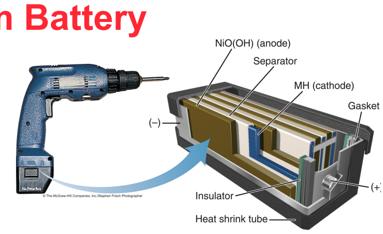
Cathode (+):

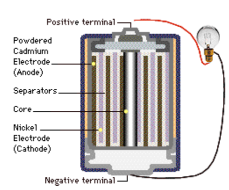
$NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$

Overall cell:

$2 NiO(OH) + 2 H_2O + Cd \rightarrow 2 Ni(OH)_2 + Cd(OH)_2$

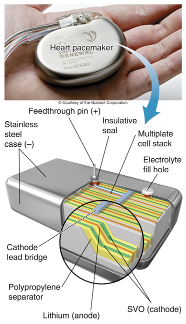
$E_{cell} = 1.4$ V





MAR

Lithium Battery



The primary lithium battery is widely used in watches, implanted medical devices, and remote-control devices.

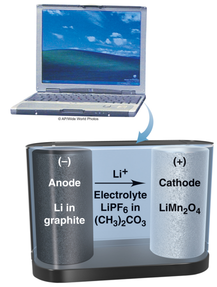
Anode (oxidation):
$3.5Li(s) \rightarrow 3.5Li^{+} + 3.5e^{-}$

Cathode (reduction):
$AgV_2O_{5.5} + 3.5Li^{-} + 3.5e^{-} \rightarrow Li_{3.5}V_2O_{5.5}$

Overall (cell) reaction:
$AgV_2O_{5.5} + 3.5Li(s) \rightarrow Li_{3.5}V_2O_{5.5}$

MAR

Lithium-Ion Battery



Anode (oxidation):
$Li_xC_6(s) \rightarrow xLi^{+} + xe^{-} + C_6(s)$

Cathode (reduction):
$Li_{1-x}Mn_2O_4(s) + xLi^{+} + xe^{-} \rightarrow LiMn_2O_4(s)$

Overall (cell) reaction:
$Li_xC_6(s) + Li_{1-x}Mn_2O_4(s) \rightarrow LiMn_2O_4(s)$

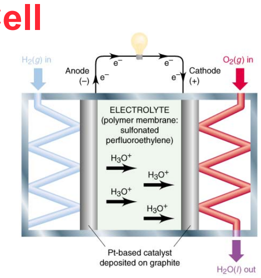
$E_{cell} = 3.7$ V

The secondary (rechargeable) lithium-ion battery is used to power laptop computers, cell phones, and camcorders.

MAR

Hydrogen Fuel Cell

In a **fuel cell** reactants enter the cell and products leave, generating electricity through controlled combustion.
Reaction rates are lower in fuel cells than in other batteries, so an ***electrocatalyst*** is used to decrease the activation energy.



Anode (oxidation): $2H_2(g) \rightarrow 4H^{+}(aq) + 4e^{-}$

Cathode (reduction): $O_2(g) + 4H^{+}(aq) + 4e^{-} \rightarrow 2H_2O(g)$

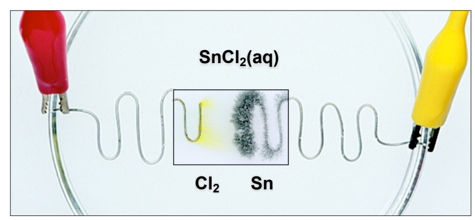
Overall (cell) reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ $E_{cell} = 1.2$ V

MAR

Electrolysis

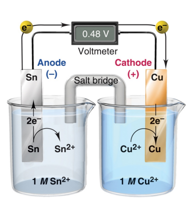
Using external electrical energy to produce chemical change in a nonspontaneous reaction

$Sn^{2+}(aq) + 2\,Cl^{-}(aq) \longrightarrow Sn(s) + Cl_2(g)$



MAR

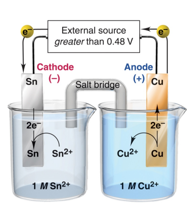
A tin-copper reaction as a voltaic and electrolytic cell



$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^{-}$
$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

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

voltaic *cell,* $E_{cell} = 0.48$ V



$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$
$Sn^{2+}(aq) + 2e^{-} \rightarrow Sn(s)$

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

electrolytic *cell,* $E_{cell} = -0.48$ V

MAR

Electrolysis of Aqueous NaOH

Electric Energy ----> Chemical Change

Anode (+) $E^o = -0.40$ V

$4\,OH^{-} \longrightarrow O_2(g) + 2\,H_2O + 2e^{-}$

Cathode (-) $E^o = -0.83$ V

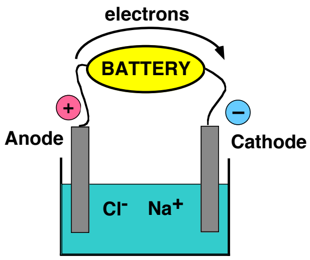
$4\,H_2O + 4e^{-} \longrightarrow 2\,H_2 + 4\,OH^{-}$

E^o for cell = -1.23 V

MAR

Electrolysis

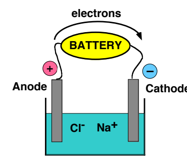
Electric Energy ---> Chemical Change



Electrolysis of molten NaCl. Here a battery "pumps" electrons from Cl^- to Na^+. Polarity of electrodes is reversed from batteries.

MAR

Electrolysis of Molten NaCl



Anode (+) $E^o = -1.36$ V

$2\ Cl^- \rightarrow Cl_2(g) + 2e^-$

Cathode (-) $E^o = -2.71$ V

$Na^+ + e^- \rightarrow Na$

E^o for cell = -4.07 V

External energy needed because E^o is (-).

MAR

Electrolysis of Aqueous NaCl

Anode (+) $E^o = -1.36$ V

$2\ Cl^- \rightarrow Cl_2(g) + 2e^-$

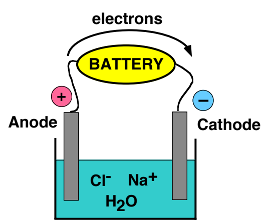
Cathode (-) $E^o = -0.83$ V

$2\ H_2O + 2e^- \rightarrow H_2 + 2\ OH^-$

E^o for cell = -2.19 V

Note that H_2O is more easily reduced than Na^+.

Also, Cl^- is oxidized in preference to H_2O because of kinetics.



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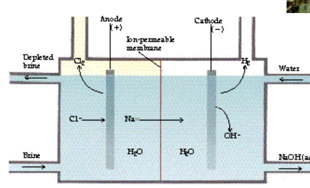
Electrolysis of Aqueous NaCl

Cells like these are the source of NaOH and Cl_2.

In 2006

65 million tons Cl_2

81 million tons NaOH



Also the source of NaOCl for use in bleach.

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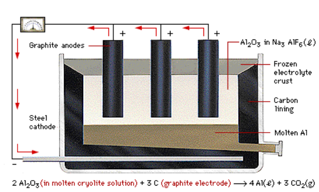
Producing Aluminum

$2\ Al_2O_3 + 3\ C \rightarrow 4\ Al + 3\ CO_2$



Charles Hall (1863-1914) developed electrolysis process, founded Alcoa *(alcoa.com)*

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See:

- *Chapter Seventeen Study Guide*
- *Chapter Seventeen Concept Guide*
- *Types of Equilibrium Constants*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*

End of Chapter 17

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Important Equations, Constants, and Handouts from this Chapter:

Redox Reactions: oxidation, reduction, LEO, GER, oxidizing agent, reducing agent, anode, cathode, galvanic/voltaic cells, electrolysis (electrolytic cells), shorthand notation for galvanic cells, SHE electrode

- **know how to balance redox reactions in acid or base conditions**
- **be able to calculate E° and E for cells**

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

$$\text{Amps} = \frac{\text{coulombs}}{\text{seconds}}$$

$$E = E^\circ - (RT/nF)\ln Q$$

R = 8.3145 J mol^{-1} K^{-1}

F = 9.6485 x 10^{4} C/mol e^{-}

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

Handouts:

- *Thermodynamic Values and Electrochemical Cell Values (Problem Set #5)*

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End of Chapter Problems: *Test Yourself*

You will need the table of reduction potentials found in problem set #5

1. Write a balanced equation for the following half-reaction: **VO_3^{-1}(aq) → V^{2+}(aq) (in acid)**
2. Write a balanced equation for the following half-reaction: **Ag(s) → Ag_2O(s) (in base)**
3. Balance the following redox equation in acid: **Zn(s) + NO_3^{-1}(aq) → Zn^{2+}(aq) + N_2O(g)**
4. Balance the following redox equation in base: **CrO_4^{2-}(aq) + SO_3^{2-}(aq) → $Cr(OH)_3$(s) + SO_4^{2-}(aq)**
5. Balance the following *unbalanced* equation in acid, then calculate the standard redox potential, *E°*: **Cu(s) + NO_3^{-1}(aq) → Cu^{2+}(aq) + NO(g)**
6. Calculate *E°*, Δ*G°* and the equilibrium constant for the following reaction: 2 Fe^{3+}(aq) + 2 I^{-1}(aq) → 2 Fe^{2+}(aq) + I_2(aq)

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End of Chapter Problems: *Answers*

1. VO_3^{-}(aq) + 6 H^{+}(aq) + 3 e^{-} → V^{2+}(aq) + 3 H_2O(l)
2. 2 Ag(s) + 2 OH^{-}(aq) → Ag_2O(s) + H_2O(l) + 2 e^{-}
3. 4 Zn(s) + 2 NO_3^{-}(aq) + 10 H^{+}(aq) → 5 H_2O(l) + 4 Zn^{2+}(aq) + N_2O(g)
4. 2 CrO_4^{2-}(aq) + 5 H_2O(l) + 3 SO_3^{2-}(aq) → 2 $Cr(OH)_3$(s) + 4 OH^{-}(aq) + 3 SO_4^{2-}(aq)
5. 3 Cu(s) + 2 NO_3^{-1}(aq) + 8 H^{+}(aq) → 2 NO(g) + 3 Cu^{2+}(aq) + 4 H_2O(l), *E°* = 0.62 V
6. *E°* = 0.236 V, Δ*G°* = -45.5 kJ, K = 9 x 10^{7}

You will need the table of reduction potentials found in problem set #5

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