

Chapter 18: Electrochemistry

The interconversion of chemical and electrical energy through oxidation-reduction.

Important for:

- Production of batteries
- Electroplating
- Corrosion protection
- Forcing reactions in "nonspontaneous" directions



Two major electrochemical types:

Voltaic (galvanic) cells:

Using spontaneous chemical reactions to do work (i.e. provide electricity).

Electrolytic Cells:

Using electricity to force nonspontaneous reactions.

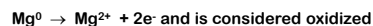


Voltaic Cells

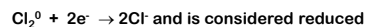
General Idea:

Since redox reactions involve the transfer of electrons from one component of a reaction to another, intercepting that transfer (flow) of electrons, allows useful "work" to be done (i.e. electrical circuits can be powered).

Ex. $\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2$ In this example magnesium loses two electrons and each chlorine gains an electron



This is the oxidation half-reaction. It only shows the component oxidized and does not include any spectator ions.



This is the reduction half-reaction. It only shows the component reduced and does not include any spectator ions.

- What type of reaction is this?
- What happens to the zinc?
- What happens to the copper ions?
- What would the nitrate ion be considered?
- What is the oxidation half reaction?
- What is the reduction half reaction?

Recall: Electrons that are gained go on the left side of the reaction arrow. Electrons that are lost go on the right.

•How do you know whether or not a redox reaction will occur spontaneously?

•Any metallic species in the *activity series* can reduce any metallic ion listed to its right. This is based on the "strength" of the metal to give up its electrons.



Don't Forget: **Leo Goes Ger**
Loses Electrons Oxidized
Gains Electrons Reduced

TABLE 16.1 Standard Reduction Potentials at 25°C Standard conditions are: 1M solutions, 1 atm for gases and a temperature of 25°C.

Reduction Half-Reaction	E° (V)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.36
$CeO_2^{2+}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Ce^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	-0.13
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.26
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	-0.40
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.45
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.37
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04

Stronger oxidizing agent ↑
Weaker oxidizing agent ↓
Weaker reducing agent ↓
Stronger reducing agent ↑

Let's examine a magnesium/cupric nitrate demonstration.

•What are some indicators that a reaction is taking place?

Electrons transferred from magnesium to copper

•Write the overall reaction, then write the oxidation half-reaction and the reduction half-reaction.

•What would happen if you place copper into a magnesium nitrate solution?

•Could you have predicted using an activity series (lab manual p.20) that this reaction would take place?

Answer:

$$Mg_{(s)} + Cu(NO_3)_2(aq) \rightarrow Mg(NO_3)_2(aq) + Cu_{(s)}$$

OHR: $Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^-$

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

Nothing would happen if you put copper in magnesium nitrate solution

Activity series predicts this reaction. Magnesium is a more active metal than copper.

What would happen if we separated the magnesium metal from the copper nitrate solution but connected them with a wire between them?

This is the rudimentary basis for a voltaic (galvanic) cell.

•Which way would the electrons flow?

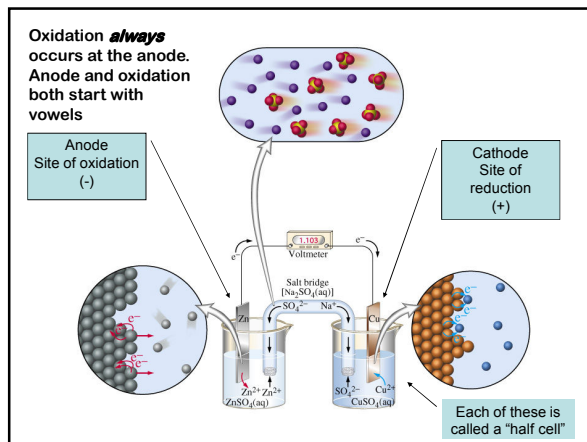
•How could this be used to do useful work?

•What is the fundamental flaw with this design?

Answer: The charge build up would prevent the reaction from progressing very far.

A method must be used to keep the reaction electrically "neutral".

This is the purpose of an electrochemical (voltaic) cell.



Calculating the Potential (voltage) for a Voltaic Cell

A table of *standard reduction (half-cell) potentials* must be used (p 481; lab book p.30)

The standard cell voltage (emf or electromotive force) for an electrochemical cell is

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} + E^{\circ}_{\text{ox}} \quad \text{or} \quad E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

(This one doesn't require you to flip the sign)

Don't forget, the table is a "reduction potential" table, so if you want oxidation you have to flip the sign on the number.

Using your table, calculate the cell potential for the Zn/Zn²⁺, Cu/Cu²⁺ cell on the previous slide.

TABLE 18.1 Standard Reduction Potentials at 25°C		Standard conditions are: 1M solutions, 1 atm for gases and a temperature of 25°C.	
Reduction Half-Reaction	E° (V)		
F ₂ (g) + 2 e ⁻ → 2 F ⁻ (aq)	2.87	Weaker oxidizing agent ↑	
H ₂ O ₂ (aq) + 2 H ⁺ (aq) + 2 e ⁻ → 2 H ₂ O(l)	1.78		
MnO ₄ ⁻ (aq) + 8 H ⁺ (aq) + 5 e ⁻ → Mn ²⁺ (aq) + 4 H ₂ O(l)	1.51		
Cl ₂ (g) + 2 e ⁻ → 2 Cl ⁻ (aq)	1.36		
Cr ₂ O ₇ ²⁻ (aq) + 14 H ⁺ (aq) + 6 e ⁻ → 2 Cr ³⁺ (aq) + 7 H ₂ O(l)	1.33		
O ₂ (g) + 4 H ⁺ (aq) + 4 e ⁻ → 2 H ₂ O(l)	1.23		
Br ₂ (l) + 2 e ⁻ → 2 Br ⁻ (aq)	1.09		
Ag ⁺ (aq) + e ⁻ → Ag(s)	0.80		
Fe ³⁺ (aq) + e ⁻ → Fe ²⁺ (aq)	0.77		
O ₂ (g) + 2 H ⁺ (aq) + 2 e ⁻ → H ₂ O ₂ (aq)	0.70		
I ₂ (s) + 2 e ⁻ → 2 I ⁻ (aq)	0.54		
O ₂ (g) + 2 H ₂ O(l) + 4 e ⁻ → 4 OH ⁻ (aq)	0.40		
Cu ²⁺ (aq) + 2 e ⁻ → Cu(s)	0.34		
Sr ²⁺ (aq) + 2 e ⁻ → Sr(s)	0.15		
2 H⁺(aq) + 2 e⁻ → H₂(g)	0		
Pb ²⁺ (aq) + 2 e ⁻ → Pb(s)	-0.13		↓ Stronger reducing agent
Ni ²⁺ (aq) + 2 e ⁻ → Ni(s)	-0.26		
Cd ²⁺ (aq) + 2 e ⁻ → Cd(s)	-0.40		
Fe ²⁺ (aq) + 2 e ⁻ → Fe(s)	-0.45		
Zn ²⁺ (aq) + 2 e ⁻ → Zn(s)	-0.76		
2 H ₂ O(l) + 2 e ⁻ → H ₂ (g) + 2 OH ⁻ (aq)	-0.83		
Al ³⁺ (aq) + 3 e ⁻ → Al(s)	-1.66		
Mg ²⁺ (aq) + 2 e ⁻ → Mg(s)	-2.37		
Na ⁺ (aq) + e ⁻ → Na(s)	-2.71		
Li ⁺ (aq) + e ⁻ → Li(s)	-3.04		

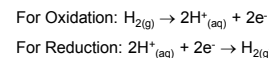
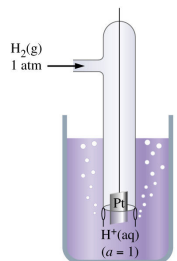
Answer:

$$E^{\circ}_{\text{Cell}} = .339\text{V} + 0.762\text{V} = 1.101\text{V}$$

Standard Hydrogen Electrode (SHE)

Reference Electrode = 0.00V by international agreement
"Standard" conditions: gases = 1 atm (~1bar); solutions = 1M

Values usually given at 298K (25°C)



Examples:

If the zinc half-cell is put together with the copper half-cell the expected voltage is:

SRP:
 $\text{Cu} = +.340\text{V}$ $\text{Zn} = -.763\text{V}$

$E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}}$ or $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

$E^\circ_{\text{cell}} = .340\text{V} + .763\text{V} = +1.103\text{V}$

Condensed (abbreviated) Cell Diagram

Anode Salt bridge Cathode

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

Half-cell (oxidation) Half-cell (reduction)

Note that the anode (oxidation) is listed on the left. A single vertical line represents a phase boundary and the double vertical line indicates the salt bridge. Normally spectator ions are not shown.

More complex abbreviated cell notations

$\text{Pt} | \text{Cl}^-, \text{Cl}_2 || \text{NO}_3^-, \text{NO} | \text{Pt}$

Platinum Electrode Species in the same phase

$\text{Pt} | \text{I}^- | \text{I}_2 || \text{Br}_2 | \text{Br}^- | \text{Pt}$

Ion Crystal Liquid Ion

Oxidation (or reduction) species in different phases

Question:

Draw a full cell diagram, a condensed cell diagram and determine the cell potential for a combination of silver/silver nitrate and aluminum/aluminum nitrate. Use sodium nitrate paste as the salt bridge. Also, identify the direction of electron flow and label the anode and the cathode.

Finally, write the net ionic equation for the reaction.

Answer:

Draw a full cell diagram, a condensed cell diagram and determine the cell potential for a combination of silver/silver nitrate and aluminum/aluminum nitrate. Use sodium nitrate paste as the salt bridge. Also, identify the direction of electron flow and label the anode and the cathode.

Finally, write the net ionic equation for the reaction.

$\text{Al}_{(\text{s})} + 3\text{Ag}^+_{(\text{aq})} \rightarrow \text{Al}^{3+}_{(\text{aq})} + 3\text{Ag}_{(\text{s})}$

$\text{Al}_{(\text{s})} | \text{Al}^{3+}_{(\text{aq})} || \text{Ag}^+_{(\text{aq})} | \text{Ag}_{(\text{s})}$ $E^\circ_{\text{cell}} = +0.80\text{v} - (-1.66\text{V}) = 2.46\text{V}$

Concentration Cells

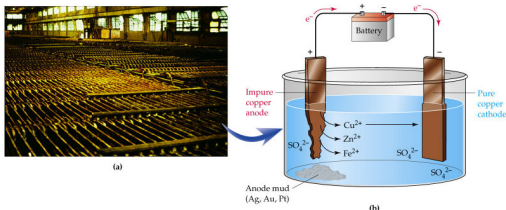
A potential difference can be created with two half-cells having the same metals in solutions containing their ions if there is a molarity difference between the two solutions.

Explained via Le Chatelier's Principle: A chemical system will react in such a way as to reduce any stress placed upon that system.

What would happen if you had two copper nitrate solutions with copper electrodes but one solution was .025M and the other was 1.50M?

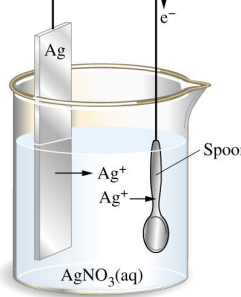
Electrolysis

Using electrical energy to drive a reaction in a nonspontaneous direction.



Purification of copper process
Copper ions are more "reducible" than zinc or iron ions

Electroplating: Plating a more "precious" metal onto the surface of a base metal or other object.



Important Note: In electrolytic cells, the anode is still the site of oxidation (as always), but is considered to be positive (+), while the cathode is negative (-).

In the schematic of the battery in the diagram (the series of long and short vertical lines [that represent battery "cells"], the long line at the outer edge is positive and the short line at the opposite outer edge is negative.

Current and time

Charge

Moles of e⁻

Moles of product

Grams or liters of product

Current, Voltage and Electrochemistry

Faraday Constant (F) = 96,480 C/mol e⁻
Gives the amount of charge (in coulombs) that exist in 1 mole of electrons passing through a circuit.

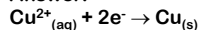
Another Useful Equation:
Ohm's Law: $V = I \times R$
(Also written as $E = I \times R$)
Where V (or E) = voltage (electrical potential)
I is current (in amperes (coulomb/sec))
And R is the resistance (in ohms)

1volt = 1joule/coulomb

Example problem:

How many grams of copper are deposited on the cathode of an electrolytic cell if an electric current of 2.00A is run through a solution of CuSO₄ for a period of 20min? Cu = 63.55g/mol; F = 96,480 C/mol e⁻

Answer:



$$2.00\text{A} = 2.00\text{C/s}$$

$$20\text{min} (60\text{s/min}) = 1200\text{s}$$

$$\text{Coulombs from e}^{-} = (2.00\text{C/s})(1200\text{s}) = 2400\text{C}$$

$$\text{mol e}^{-} = (2400\text{C})(1\text{mol}/96,480\text{C}) = .025\text{mol}$$

$$(.025\text{mol e}^{-})(1\text{mol Cu}/2\text{mol e}^{-}) = .0125\text{mol Cu}$$

$$\text{g Cu} = (.0125\text{mol Cu})(63.55\text{g/mol}) = .79\text{g}$$

Example problem:

How many hours would it take to produce 75.0g of metallic chromium by the electrolytic reduction of Cr³⁺ with a current of 2.25A?
Cr = 52.0g/mol; F = 96,480 C/mole⁻

Answer:

$$75.0\text{g Cr}/(52.0\text{g/mol}) = 1.44\text{mol Cr}$$

$$\text{mol e}^{-} = (1.44\text{mol Cr})(3\text{mol e}^{-}/1\text{mol Cr}) = 4.32\text{mol e}^{-}$$

$$\text{Coulombs} = (4.32\text{mol e}^{-})(96,480\text{C/mol}) = 416,793.6\text{C} (4.17 \times 10^5\text{C})$$

$$\text{Seconds} = (4.17 \times 10^5\text{C})/(2.25\text{C/s}) = 1.85 \times 10^5\text{s}$$

$$\text{Hours} = (1.85 \times 10^5\text{s})(1\text{hr}/3600\text{s}) = 51.5 \text{ hours}$$

Method of Solution

Grams → Moles

x Number of electrons per atom

x Faraday Constant
(96,480C/mol e⁻)

÷ Current (charge/time)

Seconds → Hours

Electrolysis Example:

Calcium metal can be obtained by the direct electrolysis of molten CaCl_2 , at a voltage of 3.2V.

a. How many joules of electrical energy are required to obtain 12.0lbs of calcium (453.59g/ 1 lb) (Ca = 40.08g/mol)

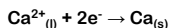
b. What is the cost of the electrical energy obtained in question "a" if the electrical energy is sold at the rate of nine cents per kilowatt hour?

kWh \rightarrow joules (J)
 kW = 1,000J/s
 1hr = 3,600s
1kWh = (1,000J/s)(3,600s) = 3.6x10⁶J

Calcium metal can be obtained by the direct electrolysis of molten CaCl_2 , at a voltage of 3.2V.
 a. How many joules of electrical energy are required to obtain 12.0lbs of calcium (453.59g/ 1 lb)
 b. What is the cost of the electrical energy obtained in question "a" if the electrical energy is sold at the rate of nine cents per kilowatt hour?

Answer:

a) The reduction half reaction for calcium is:



It takes 2 electrons to reduce 1 calcium ion (or 2 mol of electrons to reduce 1 mol of Ca)

$$12\text{lbs Ca (453.59g/lb)}(1\text{mol}/40.08\text{g}) = 135.8\text{mol Ca}$$

$$135.8\text{mol Ca (2mol } e^-/1\text{mol Ca)} = 271.6\text{mol } e^-$$

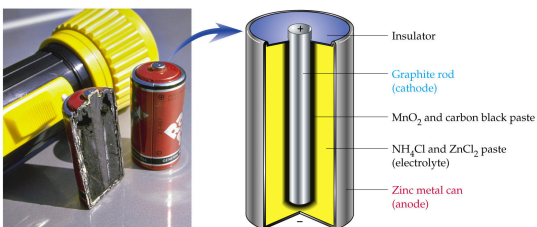
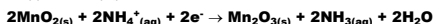
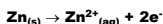
$$271.6\text{mol } e^- (96,480\text{C/mol } e^-) = 2.62 \times 10^7 \text{C}$$

$$3.2\text{V} = 3.2\text{J/C} \quad 3.2\text{J/C}(2.62 \times 10^7 \text{C}) = \mathbf{8.38 \times 10^7 \text{J}}$$

b) $8.38 \times 10^7 \text{J (9cents/kWh)} / (3.6 \times 10^6 \text{J/kWh}) = 209.5\text{cents} = \mathbf{\$2.10}$

Primary (nonrechargeable) Batteries (1.5V)

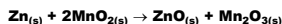
Le Clanché



Large currents cause build up of NH_3 gas at carbon cathode
 Causes voltage drop from insulation

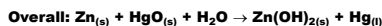
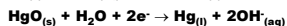
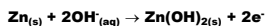
Alkaline Batteries

KOH is used instead of NH_4Cl



Does not suffer from NH_3 gas insulating the electrodes but KOH can be caustic

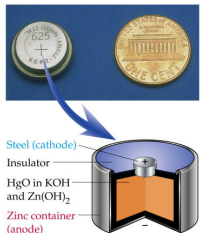
Mercury (HgO) "button" batteries (~1.3V)



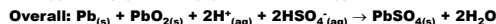
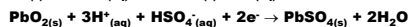
Often Ag_2O is used in place of HgO

Advantage:
 - Compact

Disadvantage:
 - Older types used mercury (a heavy metal)
 - Limited current capabilities



Lead-Acid Battery (12V)

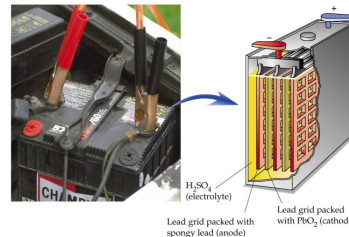


Recharging can cause electrolysis of H_2O : $2\text{H}_2\text{O}_{(l)} \rightarrow 2\text{H}_{2(g)} + \text{O}_{2(g)}$

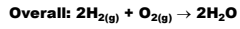
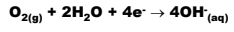
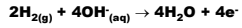
5 cells at 2.4V each

Advantages:
 -Capable of producing large currents

Disadvantages:
 -Heavy
 -Uses lead (Pb, a heavy metal)
 -Uses sulfuric acid



Fuel Cells:

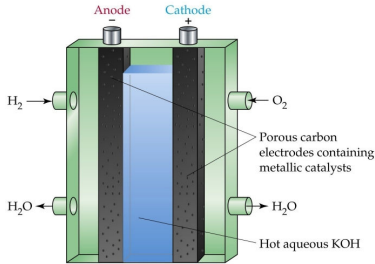


Advantages:

- "Potentially" would not use fossil fuels.
- Does not produce greenhouse gases

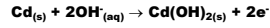
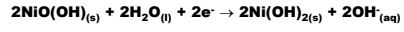
Disadvantage:

- Currently, hydrogen is derived from fossil fuels
- Hydrogen is very explosive and (currently) expensive

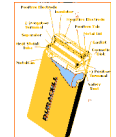


Other types of batteries:

Ni-Cad (Nickel-Cadmium)



Suffers from: weight, toxic metals and "memory"



In NiMH (Nickel-Metal Hydride)

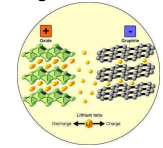
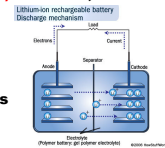
Anode consists of metal alloy (e.g. ZrNi₂)

In Li-ion (Lithium Ion) batteries, lithium ions migrate between layered materials.

Cathode = LiCoO₂

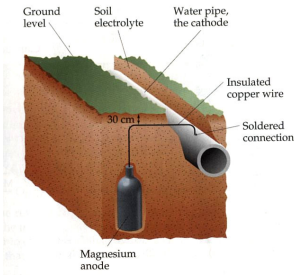
Anode = carbon

Can be prone to overheating and fires



Cathodic Protection

Using a more active metal (sacrificial anode) to protect a less active metal



◀ **Figure 20.27** Cathodic protection of an iron water pipe. The magnesium anode is surrounded by a mixture of gypsum, sodium sulfate, and clay to promote conductivity of ions. The pipe, in effect, is the cathode of a voltaic cell.