Principles of Reactivity: Electron Transfer Reactions

What is oxidation?

When a molecule/ion loses electrons (becomes more positive)

Whatever is oxidized is the reducing agent

What is reduction?

When a molecule/ion gains electrons (becomes more negative)

Whatever is reduced is the oxidizing agent

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How to Assign Oxidation Numbers

- **The oxidation state is zero for any element in its free state.**
- **The oxidation state of a monatomic ion is the electric charge on the ion. All group IA elements form ions with a single positive charge, group IIA elements form 2+ ions and the halogens form –1 ions.**
- **Fluorine always has an oxidation state of –1 in its compounds. The other halogens have oxidation states of –1 unless they are combined with a more electronegative halogen or oxygen**

Assigning Oxidation Numbers Continued

- **Hydrogen has oxidation state of +1 except when it is combined with a less electronegative element**
- **The oxidation state of oxygen is –2 except when it is bonded to fluorine (where it may be +1 or +2) and in peroxides where it has an oxidation state of –1**
- **The sum of the oxidation states of all the atoms in a molecule or ion is equal to the overall charge on the species.**

Practice Writing Oxidation States for Each Element in the Following Compounds

K_2S	$Cr_2O_7^{2-}$
NH_3	BH_3
BaO_2	MnO_4^-
Br-	ClO_3^-

Balancing Redox Equations

In redox equations, something will be oxidized and something will be reduced.

Sometimes the number of electrons that was lost in the oxidation process does not equal the number of electrons gained in the reduction process.

$\downarrow$

Therefore, we have to balance the redox equation

Rules to Balancing Redox Equations

1. Separate into two half reactions
2. Balance every element except hydrogen and oxygen
3. Balance the oxygen by adding water to the side that needs oxygens
4. Balance the hydrogens by adding H+ to the side that needs hydrogen
5. Add electrons to the more positive side such to equal to the charge on the other side

Balancing Redox Cont'd

6. Repeat steps 2-5 for the other half reaction
7. Equal the number of electrons of the two half reactions
8. Add the two half reactions
9. If the solution is in basic conditions, add the water equation

Test Your Skill

Balance the following redox equations

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

$$MnO_4^{-}(aq) + Fe^{2+} \rightarrow Fe^{3+}(s) + Mn^{2+}$$

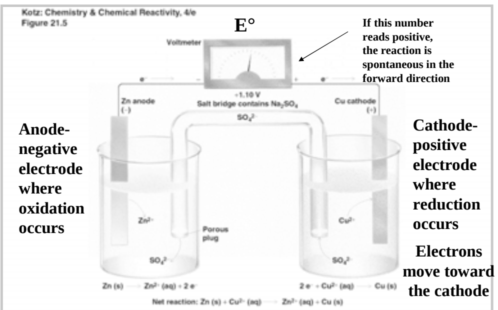
$$H_2O_2(aq) + N_2H_4(aq) \rightarrow N_2(g) + H_2O(l)$$

In basic conditions

Chemical Change Leading to an Electric Current

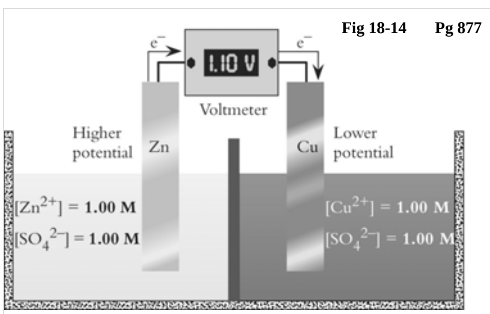
How can we take this chemical energy and convert it to electrical energy?

…With a Galvanic Cell



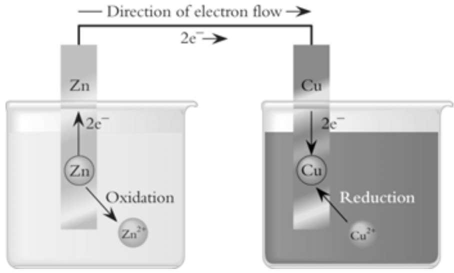
Electrodes are active

Fig 18-14 Pg 877



The copper/zinc electrochemical cell. The voltmeter measures the difference in electrical potentials between the two electrodes.

Fig 18-6 Pg 870



If the zinc-and copper-containing portions of this redox system are physically separated, electron transfer can occur only through an external wire.

Write the half reactions of the previous voltaic cell.

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2\ e^{-}$ (wire) **oxidation**

$Cu^{2+}_{(aq)} + 2\ e^{-}$ (wire) $\longrightarrow Cu_{(s)}$ **reduction**

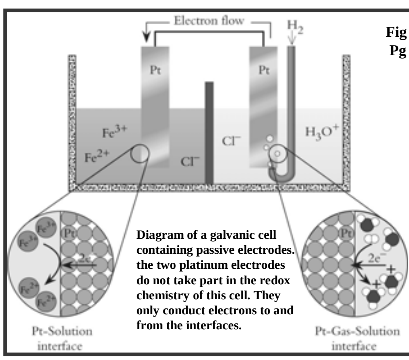


Fig 18-9
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Diagram of a galvanic cell containing passive electrodes. the two platinum electrodes do not take part in the redox chemistry of this cell. They only conduct electrons to and from the interfaces.

Electrodes are passive

Write the two half reactions

$Fe^{3+}(aq) + 1\ e^- \rightarrow Fe^{2+}(aq)$

$H_2(g) + 2\ H_2O(l) \rightarrow 2\ H_3O^+(aq) + 2e^-$

Which one occurs at the anode?

How do we calculate Standard Redox Potentials?

<u>We must compare the half reactions to a standard</u>

What is that standard?

$2\ H_3O^+(aq) + 2e^- \rightarrow H_2(g) + 2\ H_2O(l) \qquad E° = 0.00\ V$

This is called the standard hydrogen electrode or <u>SHE</u>

Now that we have a standard, we can calculate standard redox potential by using the table of standard redox potentials

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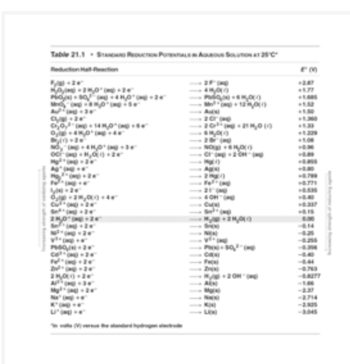


Table 21.1 • Standard Reduction Potentials in Aqueous Solution at 25°C*

Reduction Half-Reaction		$E°$ (V)
$F_2(g) + 2e^-$	$\rightarrow 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H_3O^+(aq) + 2e^-$	$\rightarrow 4H_2O(l)$	+1.77
$PbO_2(s) + SO_4^{2-}(aq) + 4H_3O^+(aq) + 2e^-$	$\rightarrow PbSO_4(s) + 6H_2O(l)$	+1.685
$MnO_4^-(aq) + 8H_3O^+(aq) + 5e^-$	$\rightarrow Mn^{2+}(aq) + 12H_2O(l)$	+1.52
$Au^{3+}(aq) + 3e^-$	$\rightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-(aq)$	+1.360
$Cr_2O_7^{2-}(aq) + 14H_3O^+(aq) + 6e^-$	$\rightarrow 2Cr^{3+}(aq) + 21H_2O(l)$	+1.33
$O_2(g) + 4H_3O^+(aq) + 4e^-$	$\rightarrow 6H_2O(l)$	+1.229
$Br_2(l) + 2e^-$	$\rightarrow 2Br^-(aq)$	+1.08
$NO_3^-(aq) + 4H_3O^+(aq) + 3e^-$	$\rightarrow NO(g) + 6H_2O(l)$	+0.96
$OCl^-(aq) + H_2O(l) + 2e^-$	$\rightarrow Cl^-(aq) + 2OH^-(aq)$	+0.89
$Hg^{2+}(aq) + 2e^-$	$\rightarrow Hg(l)$	+0.855
$Ag^+(aq) + e^-$	$\rightarrow Ag(s)$	+0.80
$Hg_2^{2+}(aq) + 2e^-$	$\rightarrow 2Hg(l)$	+0.789
$Fe^{3+}(aq) + e^-$	$\rightarrow Fe^{2+}(aq)$	+0.771
$I_2(s) + 2e^-$	$\rightarrow 2I^-(aq)$	+0.535
$O_2(g) + 2H_2O(l) + 4e^-$	$\rightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^-$	$\rightarrow Cu(s)$	+0.337
$Sn^{4+}(aq) + 2e^-$	$\rightarrow Sn^{2+}(aq)$	+0.15
$2H_3O^+(aq) + 2e^-$	$\rightarrow H_2(g) + 2H_2O(l)$	0.00
$Sn^{2+}(aq) + 2e^-$	$\rightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^-$	$\rightarrow Ni(s)$	−0.25
$V^{3+}(aq) + e^-$	$\rightarrow V^{2+}(aq)$	−0.255
$PbSO_4(s) + 2e^-$	$\rightarrow Pb(s) + SO_4^{2-}(aq)$	−0.356
$Cd^{2+}(aq) + 2e^-$	$\rightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\rightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2e^-$	$\rightarrow Zn(s)$	−0.763
$2H_2O(l) + 2e^-$	$\rightarrow H_2(g) + 2OH^-(aq)$	−0.8277
$Al^{3+}(aq) + 3e^-$	$\rightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\rightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\rightarrow Na(s)$	−2.714
$K^+(aq) + e^-$	$\rightarrow K(s)$	−2.925
$Li^+(aq) + e^-$	$\rightarrow Li(s)$	−3.045

*In volts (V) versus the standard hydrogen electrode

$E°$ means at standard state…298 K, 1 atm and 1 M of solute

Problem:

Calculate the standard redox potential for the spontaneous reaction of the following two half reactions:

$Ag^+(aq) + 1e^- \rightarrow Ag(s)$	**E° = +0.80 V**
$Na^+(aq) + 1e^- \rightarrow Na(s)$	**E° = -2.714 V**

If you ever have to multiply the half reactions to equal moles of electrons, <u>do not</u> multiply the reduction potential.

Another Problem:

Is the following reaction written spontaneous in the forward direction?

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

How does the relate to Δ*G*?

$$\Delta G° = -nFE°$$

Where
ΔG = free energy
n = number of moles of electron
***F* = Faraday's constant (9.65×10^4 J/V•mol)**
***E*= standard redox potential**

If at nonstandard state: $\Delta G = -nFE$

Electrochemical Cells at Nonstandard Conditions

As said before, the standard cell potential, E° is measured under standard conditions (298 K, 1 atm, and 1.0 M).

If we are not at standard conditions, we have to solve for *E* at nonstandard conditions

$$E = E° - (RT/\mathrm{nF}) \ln Q$$

The Nernst Equation

When temperature equals 298 K, the equation can be written:

$$E = E° - (0.0257/n) \ln Q$$

When we are at equilibrium, *E* becomes zero

$$E = 0 = E° - (0.0257/n) \ln \mathrm{K}$$

Which rearranges to

$$\frac{nE°}{0.0257} = \ln K$$

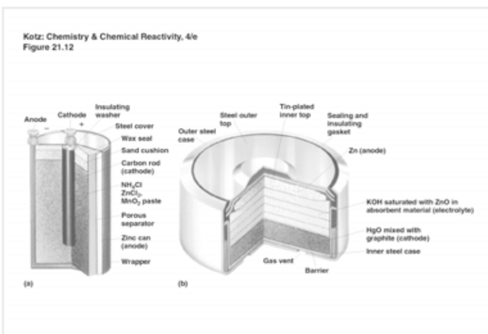
Batteries and Fuel Cells

Batteries are classified as two types:

Primary: use oxidation-reduction reactions that cannot be reversed very easily

Secondary : reactions of these batteries can be reversed (rechargeable batteries)

Primary Batteries



The Primary Batteries- Dry Cell Battery Invented by Georges Leclanché

Anode, oxidation <u>Zn Metal</u>

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

Cathode, reduction <u>Carbon Rod</u>

$$2NH_4^+(aq) + 2e^- \rightarrow 2NH_3(g) + H_2(g)$$

That is why there is MnO_2 ← **Two gases are produced that must be taken care of**

$$2MnO_2(s) + H_2 \rightarrow Mn_2O_3(s) + H_2O(l)$$

And the ammonia gas is taken up by the Zn^{2+} that was formed from the oxidation of zinc metal

$$Zn^{2+}(aq) + 2NH_3 + 2Cl^-(aq) \rightarrow Zn(NH_3)_2Cl_2(s)$$

Zinc chloride battery very similar to dry cell, but the electrolyte at the cathode is mainly $ZnCl_2$.

Three More Types of Primary Batteries

Alkaline Batteries:

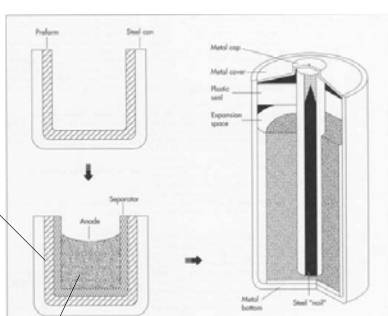
Anode, oxidation

$$Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e-$$

Cathode, reduction

$$2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(g) + 2OH^-(aq)$$

Cathode $MnO_2(s)$ and Carbon



Anode - Zn(s) and $2OH^-$

Increase storage density-- Longer Life

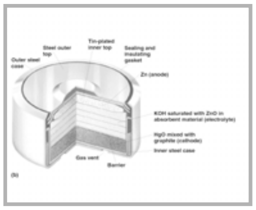
Mercury Batteries:

Anode, oxidation Zn Metal

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

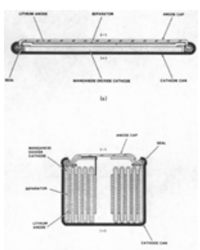
Cathode, reduction Carbon Graphite

$$HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(l) + 2OH^-(aq)$$



Lithium Batteries:

Anode Li(s) and $2OH^-$



Cathode $2MnO_2(s)$

Secondary Batteries

The primary batteries no longer produce a current when the chemicals inside have reached equilibrium conditions

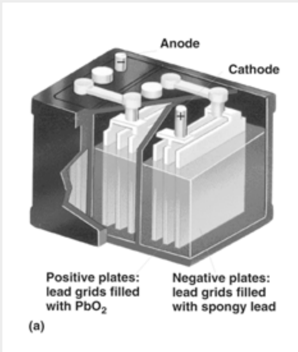
Secondary batteries can be recharged.

How?

The original reactant concentration can be restored by reversing the net cell reaction using an external source of electric energy

Lead Storage Batteries:

The battery is recharged by current from the car's alternator



Anode:

$Pb(s) + HSO_4^-(aq) + H_2O(l) \rightarrow PbSO_4(s) + H_3O^+ + 2e^-$

Cathode

$PbO_2(s) + 3H_3O^+ + 2HSO_4^- + 2e^- \rightarrow PbSO_4(s) + 5H_2O(l)$

Nickel-Cadmium Batteries

Have the advantage that the oxidizing and reducing agent can be regenerated easily

Anode: $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

Cathode: $NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$

Lithium Ion Batteries

Anode – ultrapure graphite (carbon)

Cathode – lithium cobalt oxide, nickel oxide or manganese oxide prepared with millions of tiny pores

Li+ $\longrightarrow$ **Lithium forms a complex with the metal oxide**

Requires liquid electrolytes – lithium salt in solution

Lithium Polymer Batteries

Refinement of the lithium ion battery

Integrates the electrolyte into a polymer plastic separator

Electrolysis

Use of electric current to bring about chemical change

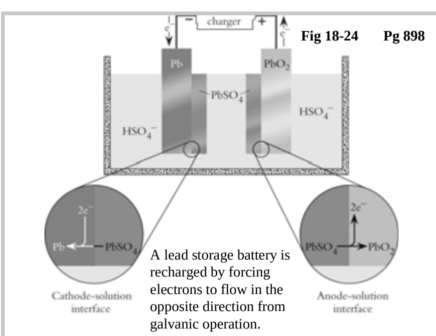


Fig 18-24 Pg 898

A lead storage battery is recharged by forcing electrons to flow in the opposite direction from galvanic operation.

The reaction can be driven in the opposite direction by an external potential of opposite sign and greater that 2.05 V.

Whether a cell operates galvanically or electrolytically, the electrode where oxidation occurs is always called the anode

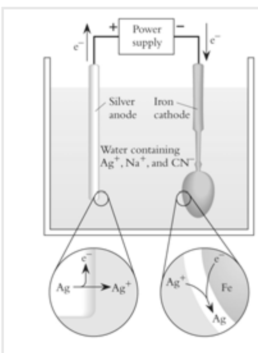


Fig 18-26 **Pg 901**

The electroplating of silver.

Pg 901

Courtesy International Silver Plating, Inc.

Electrolysis of Water

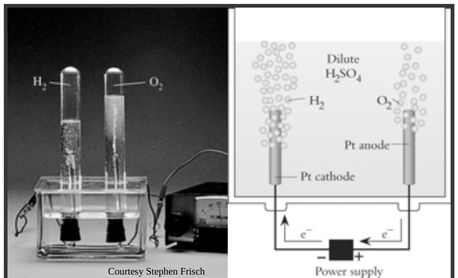


Fig 18-25 A photograph and schematic diagram of a cell for the electrolysis of water. The reaction generates hydrogen and oxygen in a 2:1 ratio.

Pg 898

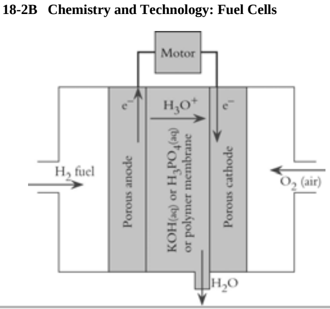
Electrolysis of Water

Anode: $6H_2O(l) \rightarrow O_2(g) + 4H_3O^+(aq) + 4e^-$

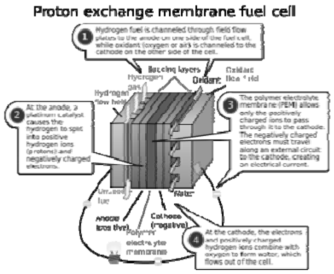
Cathode: $4H_3O^+(aq) + 4e^- \rightarrow 2H_2(g) + 4H_2O(l)$

Overall: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

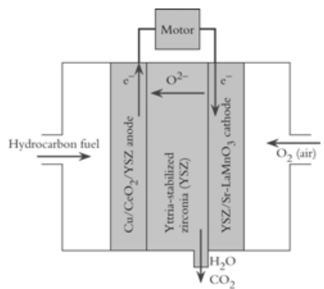
Box 18-2B Chemistry and Technology: Fuel Cells **Pg 896**



Fuel serves as the electron source and the electrodes are catalysts



Box 18-2C Chemistry and Technology: Fuel Cells Pg 896



Box 18-2D Chemistry and Technology: Fuel Cells **Pg 896**

Courtesy DaimlerChrysler Corporation