Lecture General Chemistry
Winter Term 2022/23

Dr. Lars Birlenbach
Physikalische Chemie 1 (PC1)
AR-F0102
Tel.: 0271 740 2817
eMail: birlenbach@chemie.uni-siegen.de

- Website (Slides, Excercises):
- http://www.chemie.uni-siegen.de/pc/lehre/nanoscitec/

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Reactions in aqueous solutions

- Some essential terminology
- assigning oxidation states
- Balancing redox equations

Terminology

- Oxidation
- Reduction
- Redox-Reaction
- Oxidation Number

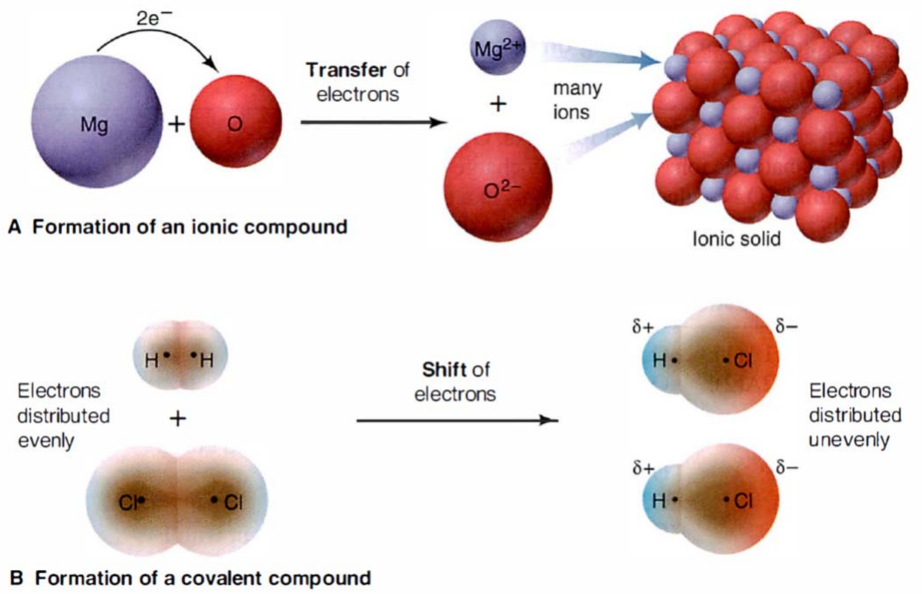


Table 4.3 Rules for Assigning an Oxidation Number (O.N.)

General Rules

1. For an atom in its elemental form (Na, O_2, Cl_2, etc.): O.N. = 0
2. For a monatomic ion: O.N. = ion charge
3. The sum of O.N. values for the atoms in a molecule or formula unit of a compound equals zero. The sum of O.N. values for the atoms in a polyatomic ion equals the ion's charge.

Rules for Specific Atoms or Periodic Table Groups

1. For Group 1A(1):	O.N. = +1 in all compounds
2. For Group 2A(2):	O.N. = +2 in all compounds
3. For hydrogen:	O.N. = +1 in combination with nonmetals
	O.N. = −1 in combination with metals and boron
4. For fluorine:	O.N. = −1 in all compounds
5. For oxygen:	O.N. = −1 in peroxides
	O.N. = −2 in all other compounds (except with F)
6. For Group 7A(17):	O.N. = −1 in combination with metals, nonmetals (except O), and other halogens lower in the group

Balancing Redox Equations

1. Write as much of the overall unbalanced equation as possible, omitting spectator ions.
2. Construct unbalanced oxidation and reduction half-reactions (these are usually incomplete as well as unbalanced). Show complete formulas for polyatomic ions and molecules.
3. Balance by inspection all elements in each half-reaction, except H and O. Then use the chart in Section 11-5 to balance H and O in each half-reaction.
4. Balance the charge in each half-reaction by adding electrons as "products" or "reactants."
5. Balance the electron transfer by multiplying the balanced half-reactions by appropriate integers.
6. Add the resulting half-reactions and eliminate any common terms.
7. Add common species that appear on the same side of the equation, and cancel equal amounts of common species that appear on opposite sides of the equation in equal amounts. The electrons must *always* cancel.
8. Check for mass balance (same number of atoms of each kind as reactants and products); check for charge balance (same total charge on both sides of the equation).

Example 11-10 Balancing Redox Equations

A useful analytical procedure involves the oxidation of iodide ions to free iodine. The free iodine is then titrated with a standard solution of sodium thiosulfate, $Na_2S_2O_3$. Iodine oxidizes $S_2O_3^{2-}$ ions to tetrathionate ions, $S_4O_6^{2-}$, and is reduced to I^- ions. Write the balanced net ionic equation for this reaction.

$$I_2 + S_2O_3^{2-} \longrightarrow I^- + S_4O_6^{2-}$$

$$I_2 \longrightarrow I^- \quad \text{(red. half-reaction)}$$

$$I_2 \longrightarrow 2I^-$$

$$I_2 + 2e^- \longrightarrow 2I^- \quad \text{(balanced red. half-reaction)}$$

$$S_2O_3^{2-} \longrightarrow S_4O_6^{2-} \quad \text{(ox. half-reaction)}$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^- \quad \text{(balanced ox. half-reaction)}$$

$$I_2 + 2e^- \longrightarrow 2I^-$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$$

$$I_2(s) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Balancing Oxygen and Hydrogen

In acidic solution: We add only H^+ or H_3O^+ (*not* OH^- in acidic solution).
In basic solution: We add only OH^- or H_2O (*not* H^+ in basic solution).

The following chart shows how to balance hydrogen and oxygen.

In *acidic* or *neutral* solution:	In *basic* solution:
To balance O	To balance O
For *each* O needed, add *one* H_2O	For *each* O needed, add *one* H_2O
and ↓ then	and ↓ then
To balance H	To balance H
For *each* H needed, add *one* H^+	For *each* H needed, add *one* H_2O to side needing H *and* add *one* OH^- to *other* side (This adds H without changing O)

Example 11-11 Balancing Net Ionic Equations (Acidic Solution)

Permanganate ions oxidize iron(II) to iron(III) in sulfuric acid solution. Permanganate ions are reduced to manganese(II) ions. Write the balanced net ionic equation for this reaction.

$$Fe^{2+} + MnO_4^- \longrightarrow Fe^{3+} + Mn^{2+}$$

$$Fe^{2+} \longrightarrow Fe^{3+} \quad \text{(ox. half-reaction)}$$

$$Fe^{2+} \longrightarrow Fe^{3+} + 1e^- \quad \text{(balanced ox. half-reaction)}$$

$$MnO_4^- \longrightarrow Mn^{2+} \quad \text{(red. half-reaction)}$$

$$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad \text{(balanced red. half-reaction)}$$

$$5(Fe^{2+} \longrightarrow Fe^{3+} + 1e^-)$$

$$1(MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O)$$

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(\ell)$$

Example 11-13 Balancing Redox Equations (Basic Solution)

In basic solution, hypochlorite ions, ClO^-, oxidize chromite ions, CrO_2^-, to chromate ions, CrO_4^{2-}, and are reduced to chloride ions. Write the balanced net ionic equation for this reaction.

$$CrO_2^- + ClO^- \longrightarrow CrO_4^{2-} + Cl^-$$

$$CrO_2^- \longrightarrow CrO_4^{2-} \quad \text{(ox. half-rxn)}$$

$$CrO_2^- + 4OH^- \longrightarrow CrO_4^{2-} + 2H_2O$$

$$CrO_2^- + 4OH^- \longrightarrow CrO_4^{2-} + 2H_2O + 3e^- \quad \text{(balanced ox. half-rxn)}$$

$$ClO^- \longrightarrow Cl^- \quad \text{(red. half-rxn)}$$

$$ClO^- + H_2O \longrightarrow Cl^- + 2OH^-$$

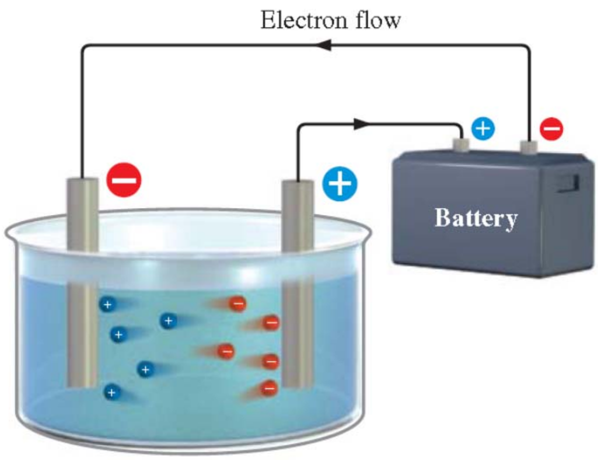
$$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^- \quad \text{(balanced red. half-rxn)}$$

$$2(CrO_2^- + 4OH^- \longrightarrow CrO_4^{2-} + 2H_2O + 3e^-)$$

$$3(ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-)$$

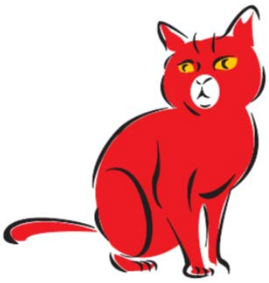
$$2CrO_2^- + 8OH^- + 3ClO^- + 3H_2O \longrightarrow 2CrO_4^{2-} + 4H_2O + 3Cl^- + 6OH^-$$

Electrochemistry

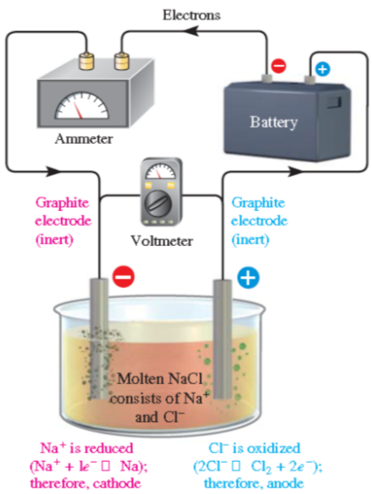


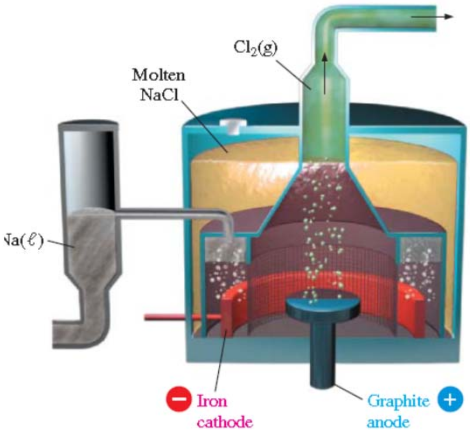
Electrodes

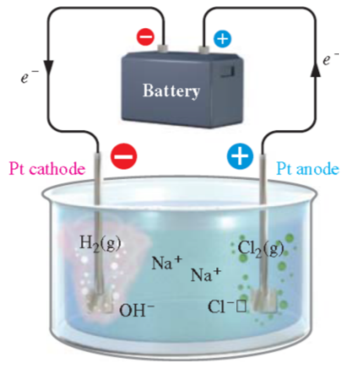
The **cathode** is defined as the electrode at which *reduction* occurs as electrons are gained by some species. The **anode** is the electrode at which *oxidation* occurs as electrons are lost by some species.



Electrolysis cells

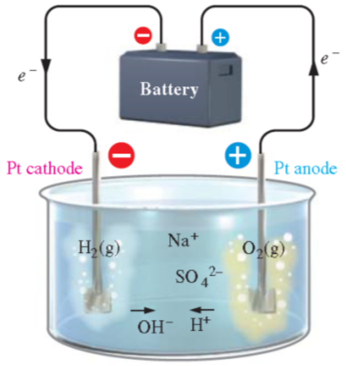






Electrolysis cells

$2Cl^- \longrightarrow Cl_2 + 2e^-$	(oxidation, anode)
$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$	(reduction, cathode)
$2H_2O + 2Cl^- \longrightarrow 2OH^- + H_2 + Cl_2$	(overall cell reaction as net ionic equation)
$+ 2Na^+ \longrightarrow + 2Na^+$	(spectator ions)
$2H_2O + 2NaCl \longrightarrow 2NaOH + H_2 + Cl_2$	(overall cell reaction as formula unit equation)



Electrolysis cells

$$
\begin{array}{rcll}
2(2H_2O + 2e^- & \longrightarrow & H_2 + 2OH^-) & \text{(reduction, cathode)} \\
2H_2O & \longrightarrow & O_2 + 4H^+ + 4e^- & \text{(oxidation, anode)} \\
\hline
6H_2O & \longrightarrow & 2H_2 + O_2 + \underbrace{4H^+ + 4OH^-}_{4H_2O} & \text{(overall cell reaction)} \\
2H_2O & \longrightarrow & 2H_2 + O_2 & \text{(net reaction)}
\end{array}
$$

Faraday's Law

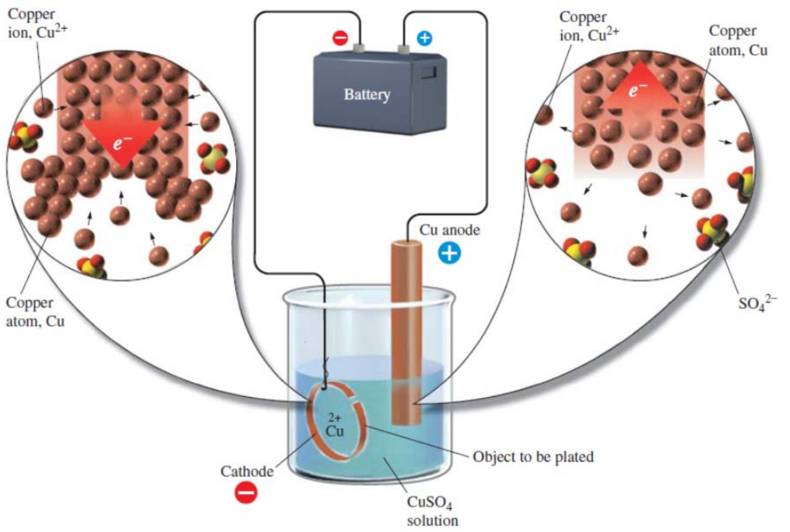
One **faraday** is the amount of electricity that corresponds to the gain or loss, and therefore the passage, of 6.022×10^{23} electrons, or *one mole* of electrons.

$$1 \text{ faraday} = 6.022 \times 10^{23}\ e^- = 96{,}485\ \text{C}$$

Table 21-1 Amounts of Elements Produced at One Electrode in Electrolysis by 1 Faraday of Electricity

Half-Reaction	Number of e^- in Half-Reaction	Product (electrode)	Amount Produced
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	1	Ag (cathode)	1 mol = 107.868 g
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	2	H_2 (cathode)	$\frac{1}{2}$ mol = 1.008 g
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	2	Cu (cathode)	$\frac{1}{2}$ mol = 31.773 g
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	3	Au (cathode)	$\frac{1}{3}$ mol = 65.656 g
$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$	2	Cl_2 (anode)	$\frac{1}{2}$ mol = 35.453 g = 11.2 L_{STP}
$2H_2O(\ell) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$	4	O_2 (anode)	$\frac{1}{4}$ mol = 8.000 g = 5.60 L_{STP}

Electroplating with copper



Lars Birlenbach birlenbach@chemie.uni-siegen.de

Voltaic (or Galvanic) Cells: The zinc-copper cell

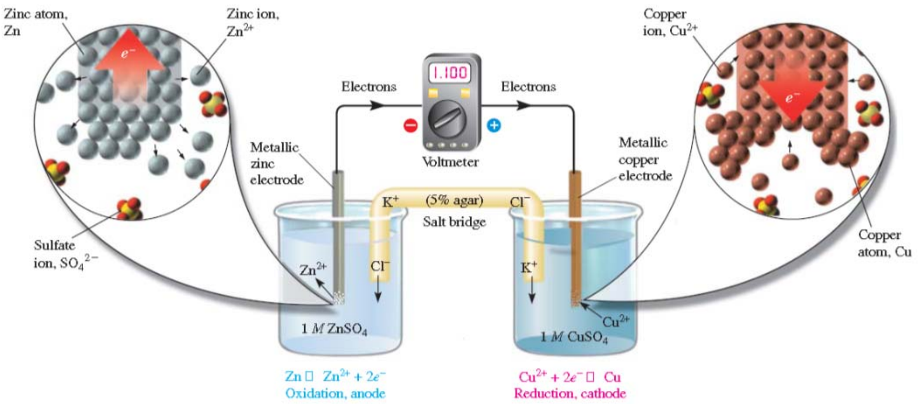
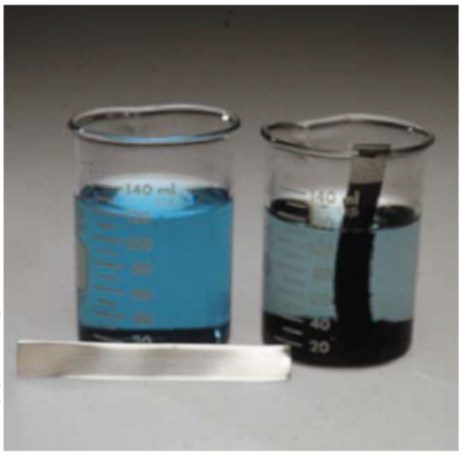


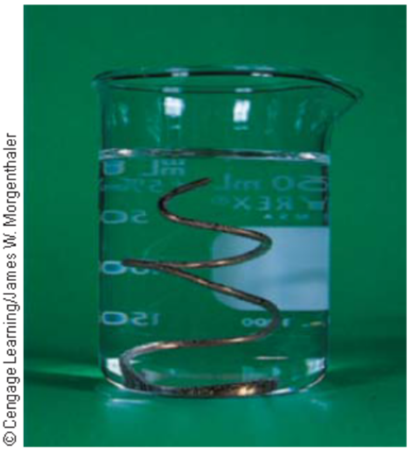
Figure 21-6 The zinc-copper voltaic cell utilizes the reaction

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

Lars Birlenbach birlenbach@chemie.uni-siegen.de

Redox potential





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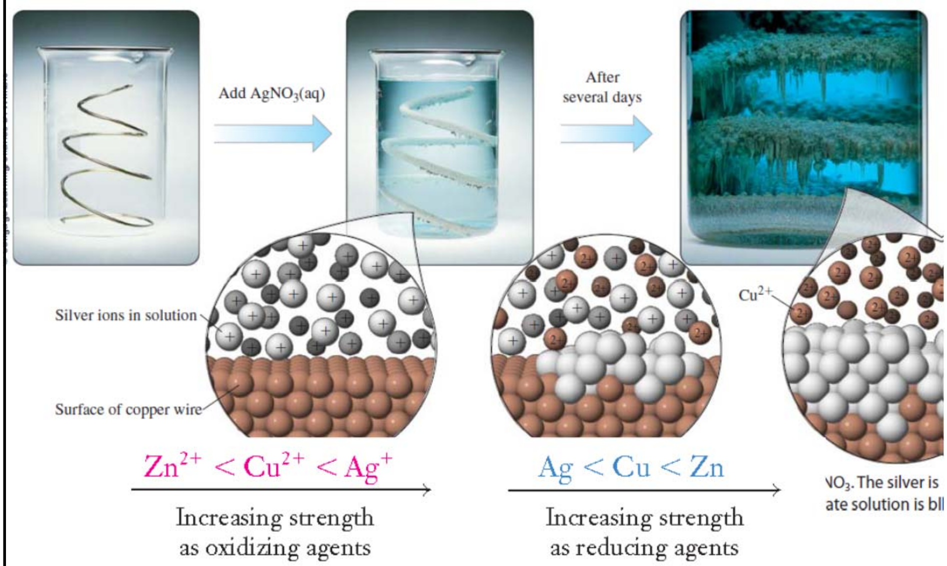

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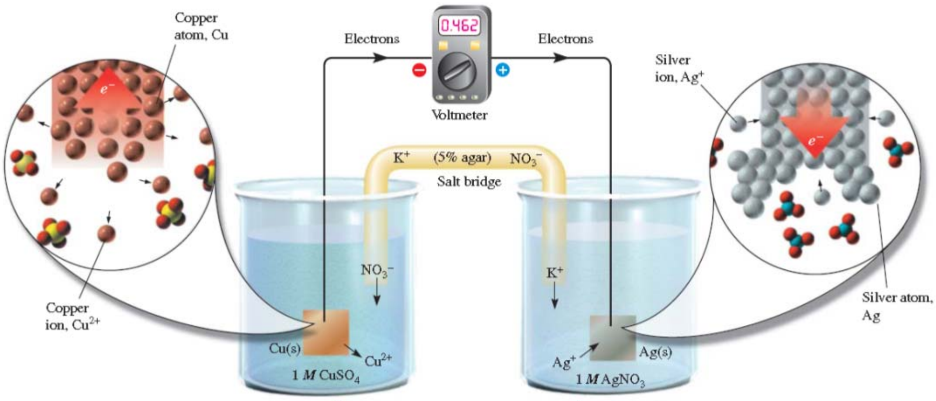
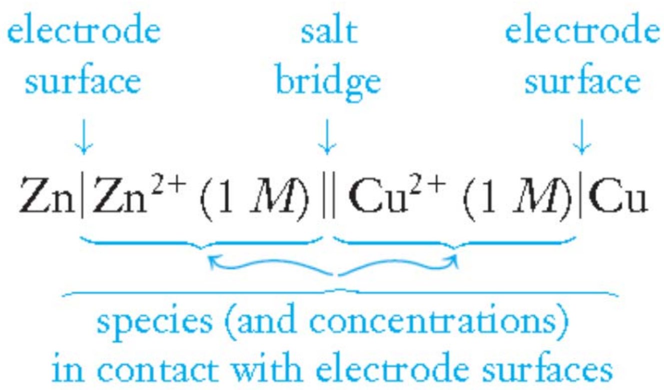
The copper-silver cell

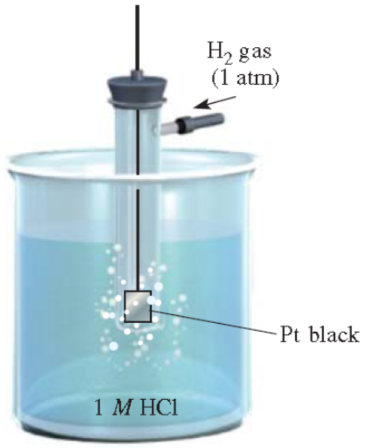


$$Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

Short notation for Voltaic Cells



Standard Electrode Potentials



By international convention, the standard hydrogen electrode (SHE) is arbitrarily assigned a potential of *exactly* 0.0000 . . . volt.

Figure 21-8 Th
electrode (SHE).
view of the ope
a cathode is sho
and as an anode in Figure 21-10.

SHE Half-Reaction	E^0 (standard electrode potential)	
$H_2 \longrightarrow 2H^+ + 2e^-$	exactly 0.0000 . . . V	(SHE as anode)
$2H^+ + 2e^- \longrightarrow H_2$	exactly 0.0000 . . . V	(SHE as cathode)

Element	Reduction Half-Reaction		Standard Reduction Potential E^0 (volts)
Li	$Li^+ + e^-$	$\longrightarrow$ Li	−3.045
K	$K^+ + e^-$	$\longrightarrow$ K	−2.925
Ca	$Ca^{2+} + 2e^-$	$\longrightarrow$ Ca	−2.87
Na	$Na^+ + e^-$	$\longrightarrow$ Na	−2.714
Mg	$Mg^{2+} + 2e^-$	$\longrightarrow$ Mg	−2.37
Al	$Al^{3+} + 3e^-$	$\longrightarrow$ Al	−1.66
Zn	$Zn^{2+} + 2e^-$	$\longrightarrow$ Zn	−0.763
Cr	$Cr^{3+} + 3e^-$	$\longrightarrow$ Cr	−0.74
Fe	$Fe^{2+} + 2e^-$	$\longrightarrow$ Fe	−0.44
Cd	$Cd^{2+} + 2e^-$	$\longrightarrow$ Cd	−0.403
Ni	$Ni^{2+} + 2e^-$	$\longrightarrow$ Ni	−0.25
Sn	$Sn^{2+} + 2e^-$	$\longrightarrow$ Sn	−0.14
Pb	$Pb^{2} + 2e^-$	$\longrightarrow$ Pb	−0.126
H_2	$2H^+ + 2e^-$	$\longrightarrow$ H_2	0.000 (reference e
Cu	$Cu^{2+} + 2e^-$	$\longrightarrow$ Cu	+0.337
I_2	$I_2 + 2e^-$	$\longrightarrow$ $2I^-$	+0.535
Hg	$Hg^{2+} + 2e^-$	$\longrightarrow$ Hg	+0.789
Ag	$Ag^+ + e^-$	$\longrightarrow$ Ag	+0.799

Increasing strength as oxidizing agent; increasing ease of reduction

Increasing strength as reducing agent; increasing ease of oxidation

Reduction Half-Reaction		Standard Reduc[tion] Potential E^0 (vo[lts])
$Zn(OH)_4^{2-} + 2e^-$	$\longrightarrow Zn + 4OH^-$	−1.22
$Fe(OH)_2 + 2e^-$	$\longrightarrow Fe + 2OH^-$	−0.877
$2H_2O + 2e^-$	$\longrightarrow H_2 + 2OH^-$	−0.828
$PbSO_4 + 2e^-$	$\longrightarrow Pb + SO_4^{2-}$	−0.356
$NO_3^- + H_2O + 2e^-$	$\longrightarrow NO_2^- + 2OH^-$	+0.01
$Sn^{4+} + 2e^-$	$\longrightarrow Sn^{2+}$	+0.15
$AgCl + e^-$	$\longrightarrow Ag + Cl^-$	+0.222
$Hg_2Cl_2 + 2e^-$	$\longrightarrow 2Hg + 2Cl^-$	+0.27
$O_2 + 2H_2O + 4e^-$	$\longrightarrow 4OH^-$	+0.40
$NiO_2 + 2H_2O + 2e^-$	$\longrightarrow Ni(OH)_2 + 2OH^-$	+0.49
$H_3AsO_4 + 2H^+ + 2e^-$	$\longrightarrow H_3AsO_3 + H_2O$	+0.58
$Fe^{3+} + e^-$	$\longrightarrow Fe^{2+}$	+0.771
$ClO^- + H_2O + 2e^-$	$\longrightarrow Cl^- + 2OH^-$	+0.89
$NO_3^- + 4H^+ + 3e^-$	$\longrightarrow NO + 2H_2O$	+0.96
$O_2 + 4H^+ + 4e^-$	$\longrightarrow 2H_2O$	+1.229
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\longrightarrow 2Cr^{3+} + 7H_2O$	+1.33
$Cl_2 + 2e^-$	$\longrightarrow 2Cl^-$	+1.360
$MnO_4^- + 8H^+ + 5e^-$	$\longrightarrow Mn^{2+} + 4H_2O$	+1.507
$PbO_2 + HSO_4^{2-} + 3H^+ + 2e^-$	$\longrightarrow PbSO_4 + 2H_2O$	+1.685

Increasing strength as oxidizing agent; increasing ease of reduction

Increasing strength as reducing agent; increasing ease of oxidation

Corrosion

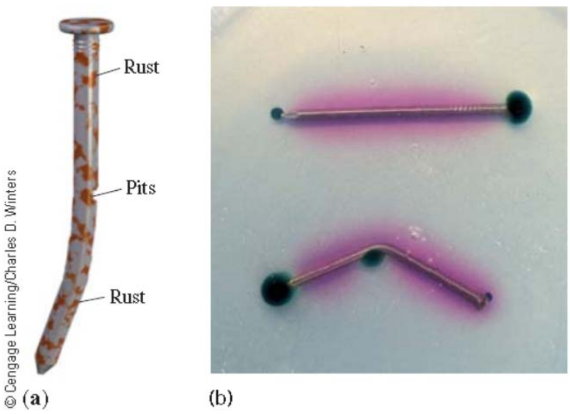
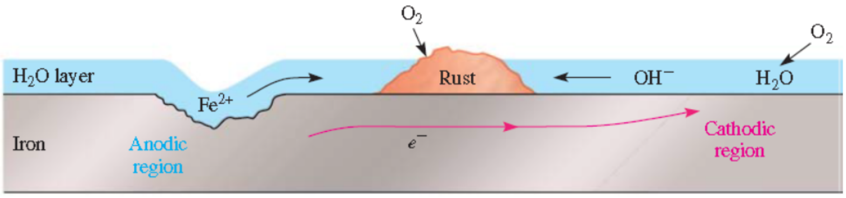


Figure 21-11 (a) A bent nail corrodes at points of strain and "active" metal atoms. (b) Two nails were placed in an agar gel that contained phenolphthalein and potassium ferricyanide, $K_3[Fe(CN)_6]$. As the nails corrode, they produce Fe^{2+} ions at each end and at the bend (an oxidation, so these are anodic regions). Fe^{2+} ions react with $[Fe(CN)_6]^{3-}$ ions to form $Fe_3[Fe(CN)_6]_2$, an intensely blue-colored compound. The rest of each nail functions as the cathode, at which water is reduced to H_2 and OH^- ions. The OH^- ions turn phenolphthalein pink.

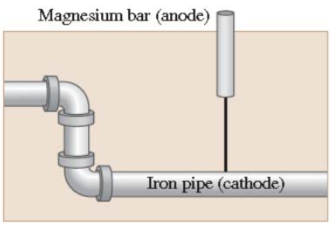
Corrosion



$$2(Fe \longrightarrow Fe^{2+} + 2e^-) \quad \text{(oxidation, anode)}$$
$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad \text{(reduction, cathod}$$
$$2Fe + O_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4OH^- \quad \text{(net reaction)}$$

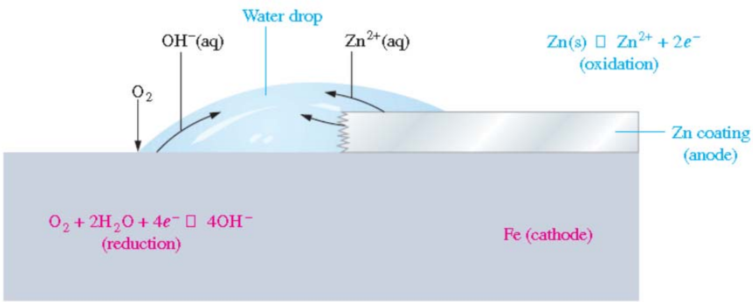
$$2Fe(s) + \tfrac{3}{2}O_2(aq) + xH_2O(\ell) \longrightarrow Fe_2O_3 \cdot xH_2O(s)$$

Corrosion protection



(a)

Corrosion protection by sacrificial anodes



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