# REDOX REACTIONS
# &
# ELECTROCHEMISTRY

# ELECTROCHEMISTRY

**Electrical energy**

↕

**Chemical energy**

**oxidation/reduction = redox reactions**

# ELECTROCHEMISTRY

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

Oxidation-reduction reactions always involve transfer of electrons from one species to another.

Species losing electrons is oxidized
Species gaining electrons is reduced

# ELECTROCHEMISTRY

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

OXIDATION: loss of electrons
REDUCTION: gain of electrons

Also change in oxidation number

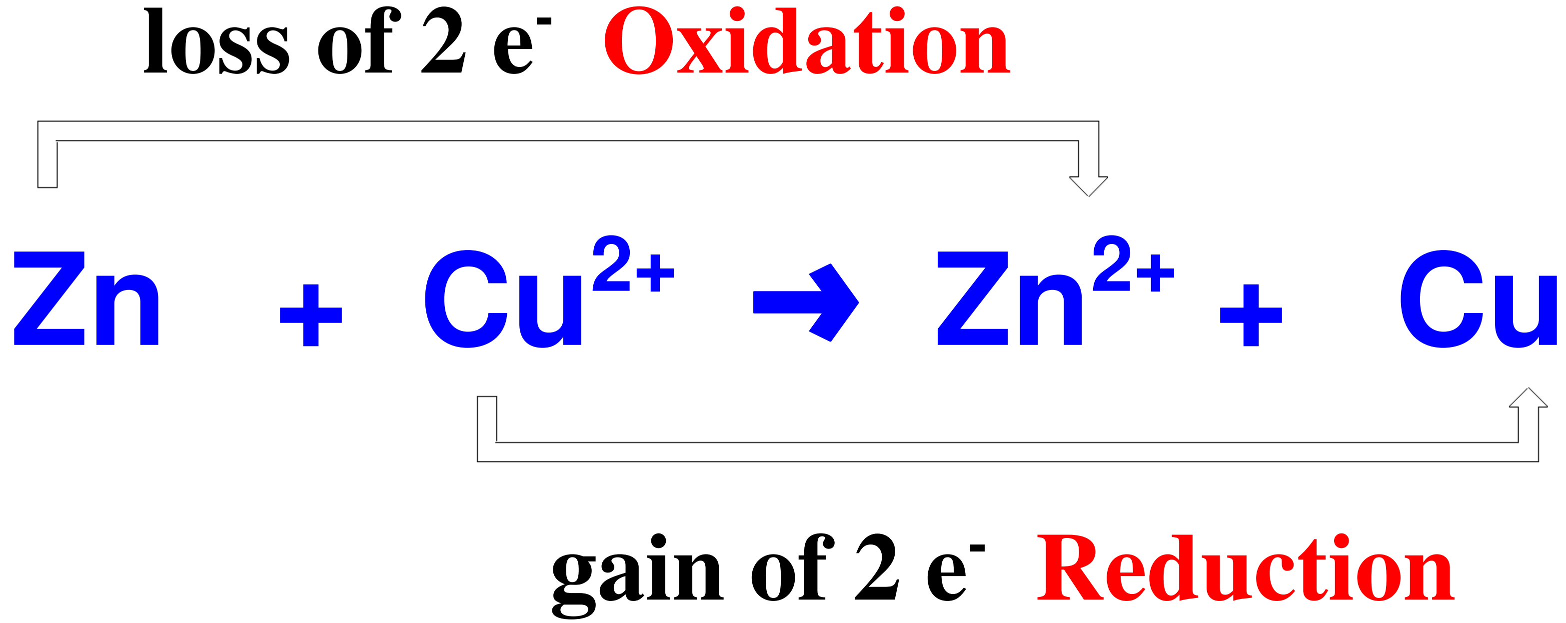
# ELECTROCHEMISTRY

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

**Oxidizing agent:** oxidizes another species; it is itself reduced.

**Reducing agent:** reduces another species; it is itself oxidized.

# ELECTROCHEMISTRY



loss of 2 $e^-$ **Oxidation**

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

gain of 2 $e^-$ **Reduction**

**Zn reducing agent**

**$Cu^{2+}$ oxidizing agent**

# ELECTROCHEMISTRY

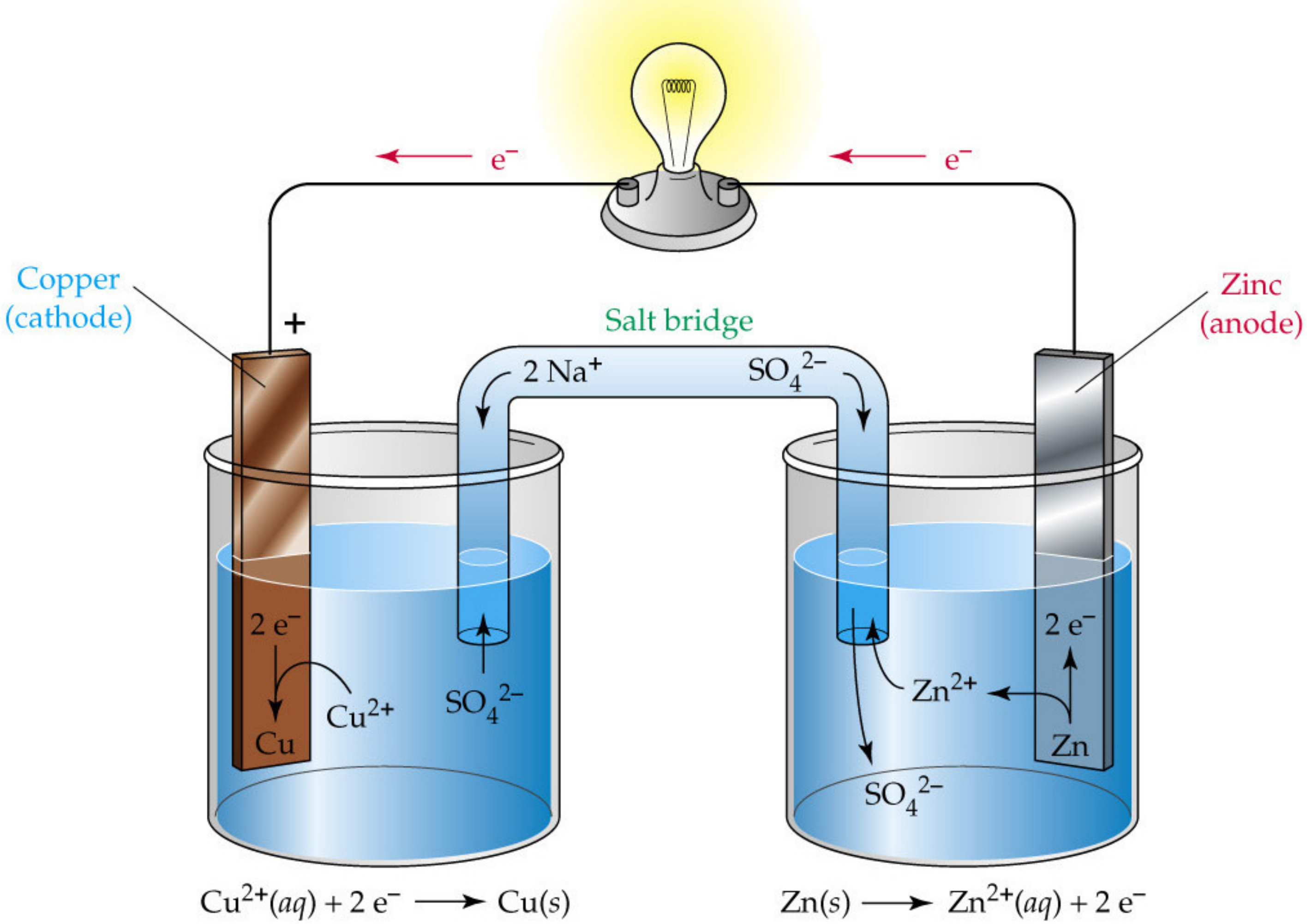
$$Mg + 2\,HCl \rightarrow MgCl_2 + H_2$$

$$Mg^0 + 2H^+Cl^- \rightarrow Mg^{2+}Cl^-_2 + H^0_2$$

Mg oxidized to $Mg^{2+}$

$H^+$ reduced to $H_2$

# ELECTROCHEMISTRY



**Chemical energy → Electrical energy**

# BALANCING REDOX EQUATIONS

$$Fe^{2+} + Cr_2O_7^{2-} \xrightarrow{acid} Fe^{3+} + Cr^{3+}$$

1. Write unbalanced ionic equation
2. Separate into half-reactions

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Oxidation

# BALANCING REDOX EQUATIONS

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1. Write unbalanced ionic equation
2. Separate into half-reactions

Reduction

# BALANCING REDOX EQUATIONS

$$Fe^{2+} + Cr_2O_7^{2-} \xrightarrow{acid} Fe^{3+} + Cr^{3+}$$

## 3. Balance where possible

$Fe^{2+} \rightarrow Fe^{3+}$ oxidation

$Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+}$ reduction

# BALANCING REDOX EQUATIONS

$$Fe^{2+} + Cr_2O_7^{2-} \xrightarrow{acid} Fe^{3+} + Cr^{3+}$$

## 4. Add water to balance oxygen

$$Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+}$$

$$Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7\,H_2O$$

# BALANCING REDOX EQUATIONS

$$Fe^{2+} + Cr_2O_7^{2-} \xrightarrow{acid} Fe^{3+} + Cr^{3+}$$

4. Add $H^+$ to balance hydrogen

$$14\,H^+ + Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7H_2O$$

5. Check charges 12+ → 6+

# BALANCING REDOX EQUATIONS

$$Fe^{2+} + Cr_2O_7^{2-} \xrightarrow{\text{acid}} Fe^{3+} + Cr^{3+}$$

4. Add $H^+$ to balance hydrogen

$$14\,H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2\,Cr^{3+} + 7H_2O$$

5. Check charges

12+ → 6+

# BALANCING REDOX EQUATIONS

$$Fe^{2+} + Cr_2O_7^{2-} \xrightarrow{acid} Fe^{3+} + Cr^{3+}$$

## 6. Compare half reactions

$$14\ H^{+} + Cr_2O_7^{2-} + 6e^{-} \rightarrow 2\ Cr^{3+} + 7H_2O$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

# BALANCING REDOX EQUATIONS

$$Fe^{2+} + Cr_2O_7^{2-} \xrightarrow{acid} Fe^{3+} + Cr^{3+}$$

## 6. Compare half reactions

$$14\,H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2\,Cr^{3+} + 7H_2O$$

$$6\,Fe^{2+} \rightarrow 6\,Fe^{3+} + 6e^-$$

# BALANCING REDOX EQUATIONS

$$Fe^{2+} + Cr_2O_7^{2-} \xrightarrow{acid} Fe^{3+} + Cr^{3+}$$

## 7. Add half reactions

$$14\ H^+ + Cr_2O_7^{2-} + \cancel{6e^-} \rightarrow 2\ Cr^{3+} + 7H_2O$$

$$6\ Fe^{2+} \rightarrow 6\ Fe^{3+} + \cancel{6e^-}$$

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$$14\ H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2\ Cr^{3+} + 7H_2O + 6\ Fe^{3+}$$

# BALANCING REDOX EQUATIONS

In basic solutions repeat steps 1-3

Add $OH^-$ both sides, 1 for each $H^+$

Combine $OH^-$ & $H^+ \rightarrow H_2O$ (eg 19.1)

# TYPES OF ELECTROCHEMICAL CELLS

**Oxidation reduction reactions separated into two half-reactions.**

**Electrochemical cell: electrodes dip into an electrolyte in which a chemical reaction either uses or generates an electric current.**

# TYPES OF ELECTROCHEMICAL CELLS

**The force with which electrons travel from the oxidation half-reaction to the reduction half-reaction is measured as voltage.**

# TYPES OF ELECTROCHEMICAL CELLS

## 1. Galvanic or Voltaic

**Spontaneous reactions**
**Produces electrical energy**

# TYPES OF ELECTROCHEMICAL CELLS

## 2. Electrolytic

Non-spontaneous reactions

Requires electrical energy

# TYPES OF ELECTROCHEMICAL CELLS

## 2. Electrolytic

**Many reactive metals obtained by electrolysis of a molten salt**

**Li, Mg, and Ca metals obtained by the electrolysis of chlorides**

# A SIMPLE EXAMPLE

$$\mathrm{Cu} + \mathrm{Ag}^{+}$$

$$\downarrow$$

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

oxidant?
reductant?

# A SIMPLE EXAMPLE

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

# Electrochemical cells

**To get better control over the system, each half-reaction placed in separate cell**

**Connected by salt bridge**

# Electrochemical cells

**oxidation at anode**

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

# Electrochemical cells

**reduction at cathode**

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

# Electrochemical cells

$$\mathrm{Zn}\,|\,\mathrm{Zn}^{2+}(1\mathrm{M})\,\|\,\mathrm{Cu}^{2+}(1\mathrm{M})\,|\,\mathrm{Cu}$$

# Standard hydrogen electrode

**Reference electrode**

**Compare to other half-cells**

$\mathbf{Pt} | \mathbf{H_2 (1atm), 1M} \|$

# Some theory

Galvanic cells push electrons through circuit.

Magnitude of this ability called potential.

Potential or electromotive force (EMF) given in volts (V).

Volt defined as amount of energy (J) per unit of charge (coulombs)

# ZINC -COPPER REACTION

E = reduction potential for a half reaction

measures how willing a species is to gain or loss electrons

Everything compared to hydrogen

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

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

$E° = +0.34V$

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

$E° = -0.76V$

|  | **Reduction Half-Reaction** |  | **E° (V)** |  |
|---|---|---|---|---|
| Stronger oxidizing agent | $F_2(g) + 2e^-$ | $\longrightarrow 2F (aq)$ | 2.87 | Weaker reducing agent |
|  | $H_2O_2(aq) + 2H^+(aq) + 2e^-$ | $\longrightarrow 2H_2O(l)$ | 1.78 |  |
|  | $MnO_4^-(aq) + 8H^+(aq) + 5e^-$ | $\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$ | 1.51 |  |
|  | $Cl_2(g) + 2e^-$ | $\longrightarrow 2Cl^-(aq)$ | 1.36 |  |
|  | $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$ | $\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ | 1.33 |  |
|  | $O_2(g) + 4H^+(aq) + 4e^-$ | $\longrightarrow 2H_2O(l)$ | 1.23 |  |
|  | $Br_2(l) + 2e^-$ | $\longrightarrow 2Br^-(aq)$ | 1.09 |  |
|  | $Ag^+(aq) + e^-$ | $\longrightarrow Ag(s)$ | 0.80 |  |
|  | $Fe^{3+}(aq) + e^-$ | $\longrightarrow Fe^{2+}(aq)$ | 0.77 |  |
|  | $O_2(g) + 2H^+(aq) + 2e^-$ | $\longrightarrow H_2O_2(aq)$ | 0.70 |  |
|  | $I_2(s) + 2e^-$ | $\longrightarrow 2I^-(aq)$ | 0.54 |  |
|  | $O_2(g) + 2H_2O(l) + 4e^-$ | $\longrightarrow 4OH^-(aq)$ | 0.40 |  |
|  | $Cu^{2+}(aq) + 2e^-$ | $\longrightarrow Cu(s)$ | 0.34 |  |
|  | $Sn^{4+}(aq) + 2e^-$ | $\longrightarrow Sn^{2+}(aq)$ | 0.15 |  |
|  | $2H^+(aq) + 2e^-$ | $\longrightarrow H_2(g)$ | 0 |  |
|  | $Pb^{2+}(aq) + 2e^-$ | $\longrightarrow Pb(s)$ | −0.13 |  |
|  | $Ni^{2+}(aq) + 2e^-$ | $\longrightarrow Ni(s)$ | −0.26 |  |
|  | $Cd^{2+}(aq) + 2e^-$ | $\longrightarrow Cd(s)$ | −0.40 |  |
|  | $Fe^{2+}(aq) + 2e^-$ | $\longrightarrow Fe(s)$ | −0.45 |  |
|  | $Zn^{2+}(aq) + 2e^-$ | $\longrightarrow Zn(s)$ | −0.76 |  |
|  | $2H_2O(l) + 2e^-$ | $\longrightarrow H_2(g) + 2OH^-(aq)$ | −0.83 |  |
|  | $Al^{3+}(aq) + 3e^-$ | $\longrightarrow Al(s)$ | −1.66 |  |
|  | $Mg^{2+}(aq) + 2e^-$ | $\longrightarrow Mg(s)$ | −2.37 |  |
|  | $Na^+(aq) + e^-$ | $\longrightarrow Na(s)$ | −2.71 |  |
| Weaker oxidizing agent | $Li^+(aq) + e^-$ | $\longrightarrow Li(s)$ | −3.04 | Stronger reducing agent |

# Calculating cell potential

**E (cell) = E (red) - E (ox)**

**using values on previous table**

**Calculate E for $Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$**

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

**RED: $Cu^{+2} + 2e^- \rightarrow Cu$**

Stronger oxidizing agent

Weaker reducing agent

| Reduction Half-Reaction | | E° (V) |
|---|---|---|
| $F_2(g) + 2e^-$ | $\longrightarrow 2F(aq)$ | 2.87 |
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| $Cu^{2+}(aq) + 2e^-$ | $\longrightarrow Cu(s)$ | 0.34 |
| $Sn^{4+}(aq) + 2e^-$ | $\longrightarrow Sn^{2+}(aq)$ | 0.15 |
| $2H^+(aq) + 2e^-$ | $\longrightarrow H_2(g)$ | 0 |
| $Pb^{2+}(aq) + 2e^-$ | $\longrightarrow Pb(s)$ | −0.13 |
| $Ni^{2+}(aq) + 2e^-$ | $\longrightarrow Ni(s)$ | −0.26 |
| $Cd^{2+}(aq) + 2e^-$ | $\longrightarrow Cd(s)$ | −0.40 |
| $Fe^{2+}(aq) + 2e^-$ | $\longrightarrow Fe(s)$ | −0.45 |
| $Zn^{2+}(aq) + 2e^-$ | $\longrightarrow Zn(s)$ | −0.76 |
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| $Al^{3+}(aq) + 3e^-$ | $\longrightarrow Al(s)$ | −1.66 |
| $Mg^{2+}(aq) + 2e^-$ | $\longrightarrow Mg(s)$ | −2.37 |
| $Na^+(aq) + e^-$ | $\longrightarrow Na(s)$ | −2.71 |
| $Li^+(aq) + e^-$ | $\longrightarrow Li(s)$ | −3.04 |

Weaker oxidizing agent

Stronger reducing agent

# Calculating cell potential

**E (cell)**

**Calculate E for Zn + $Cu^{+2}$ → $Zn^{+2}$ + Cu**

**OX: $Zn^{+2} + 2e^{-}$ → Zn(s) E = - 0.76V**

**RED: $Cu^{+2} + 2e^{-}$ → Cu E = +0.34V**

**Have to reverse Zn equation**

# Calculating cell potential

**E (cell)**

**using values on previous table**

**Calculate E for $Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$**

**OX:** $Zn^{+2} + 2e^{-} \rightarrow Zn$ **- 0.76V**
**RED:** $Cu^{+2} + 2e^{-} \rightarrow Cu$ **+0.34V**

**E** $= +0.34\,V - (-0.76\,V) = +\,1.10\,V$

# Batteries

## Portable voltaic cells

**D** chemicals in a paste or solid

**W** liquid solution

**Zinc-carbon** dry cell

1.5 V

# Batteries

## Zinc-carbon dry cell

$$Zn + 2\ MnO_2 + 2NH_4^{\ +} \rightarrow$$

$$Zn^{2+} + Mn_2O_3 + 2NH_3 + H_2O$$

# Batteries

## Lead storage cell

Large capacity and high current

Rechargeable $H_2SO_4 \rightarrow H_2O$

Density ↓ 1.2 to 1.0

Hydrometer

Cold weather: ions move slowly due to increased viscosity

# Spontaneity of redox reactions

**How is $\mathscr{E}^\circ_{cell}$ related to $\Delta G^\circ$ and K ?**

$$\Delta G^\circ = -nF\,\mathscr{E}^\circ_{cell} \qquad (1)$$

**n = moles $e^-$ transferred**

**F = Faraday constant**

**= 96,500 C/mol**

**$\Delta G^\circ$ (-) for spontaneous reaction**

$\rightarrow (+)\ \mathscr{E}^\circ_{cell}$

# Spontaneity of redox reactions

$$\Delta G^\circ = -2.3\ RT\log K \qquad (2)$$

$$-nF\,\mathcal{E}^\circ_{cell} = -2.3\ RT\log K$$

$$\mathcal{E}^\circ_{cell} = \frac{2.3\ RT\log K}{nF} \qquad (3)$$

**At 298 K and using R, F values ……**

$$\mathcal{E}^\circ_{cell} = \frac{0.0591\ \log K}{n}$$

**Use (1), (2), (3) to find variables**

# Nernst equation

**Used for non-standard conditions**

$$-nF\,\mathscr{E}^{\circ}_{cell} = -2.3\ RT\log K$$

$$\mathscr{E} = \mathscr{E}^{\circ}_{cell} - \frac{0.0591}{n} \times \log Q$$

**Q is reaction quotient**

# Corrosion

Metal deterioration due to electrochemical reactions

Iron rusting

$Fe_2O_3$    $H_2O$

$$2Fe + O_2 + 4H^+ \rightarrow$$
$$2\,Fe^{2+} + 2H_2O$$

$$\mathscr{E}° = 1.67v$$

# Corrosion

Metal deterioration due to electrochemical reactions

Silver tarnishing

$Ag \rightarrow Ag_2S$

# Corrosion

**Metal deterioration due to electrochemical reactions**

**Cu/brass**
**turning green**

**$Cu \rightarrow CuCO_3$**

# Corrosion

$$2Fe + O_2 + 4H^+ \rightarrow 2\,Fe^{2+} + 2H_2O$$

**Where does the acid come from?**

$H_2CO_3$

**$Fe^{2+}$ further oxidized by $O_2$ & $H_2O$**

**Rusting enhanced by salt water**

*(nails in water)*

**Aluminum doesn't rust** $Al_2O_3$

# Protecting metals

1. **Painting**

# Protecting metals

**2.**

**Cu, Sn, Zn on Fe**

# Protecting metals

**3.** (steel)

# Protecting metals

4. **Cathodic protection**
   **connect Fe to Zn or Mg, more easily oxidized (ship hulls)**

# Electrolysis

**Electrical energy used to make non-spontaneous reactions occur**

**Molten NaCl**

$2\ NaCl\ (l) \rightarrow 2\ Na\ (l) + Cl_2\ (g)$

# Electrolysis

**Electrical energy used to make non-spontaneous reactions occur**

**Water**

$2\ H_2O\ (l) \rightarrow 2\ H_2\ (g) + O_2\ (g)$ $\Delta G^\circ = 424$

**Anode:** $2\ H_2O \rightarrow 4H^+ + O_2 + 4e^-$

**Cathode:** $2H^+ + 2e^- \rightarrow H_2$ ×2

# Electrolysis

**Aqueous NaCl**

**What is present? $Na^+$ $Cl^-$ $H_2O$**

**2 anode reactions possible**

$$2\ H_2O \rightarrow 4H^+ + O_2 + 4e^-$$

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

**At high [$Cl^-$]: $Cl_2$ produced**

# Electrolysis

**Aqueous NaCl**

**What is present? $Na^+$ $Cl^-$ $H_2O$**

**2 cathode reactions possible**

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

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

**At high $[Cl^-]$: $Cl_2$ produced**