Chapter 11. Electrochemical Cells and Devices

Summary

- electrochemical (total) potential of ionic solution species
- electrochemical cells
- the Nernst equation for cell voltages
- thermodynamics of electrochemical cells
- batteries ($$$ …)
- industrial electrolytic processes ($$$$$$ …)
- fuel cells – important future energy sources?

Sections 11.1 to 11.3 Total Potential of Electrochemical Species

Nonelectrolyte Solution Components (***previously considered***)

For an uncharged solution component, such as water in an aqueous $CaCl_2$ solution, the **chemical potential** is

$$\mu_{H2O} = \mu_{H2O}^* + RT\ln(\gamma_{H2O}\, x_{H2O})$$

μ_{H2O}^* = chemical potential of pure water

x_{H2O} = water mole fraction

γ_{H2O} = Raoult’s law water activity coefficient = p_{H2O}/p_{H2O}^*

Ionic Solution Species

For an **ionic species**, the **total potential** $\tilde{\mu}_i$ is the sum of **chemical potential** μ_i and **electric potential energy** $z_i F \phi$.

$$\boxed{\tilde{\mu}_{\text{ion } i} = \mu_i^{\text{o}} + RT\ln(\gamma_i m_i) + z_i F \phi}$$

m_i = molality of ion *i*

γ_i = Henry's law activity coefficient of ion *i*

μ_i^{o} = chemical potential of an ideal one molal solution of ion *i*

z_i = valence of ion *i*

F = Faraday constant (96,485 coulombs per mole)

$z_i F$ = electric charge on one mole of ions of valence z_i

ϕ = electric potential

Example For one mole of Ca^{2+} ions at an electric potential of –1.5 volt, the electric potential energy is

$$z_i F\phi = (+2)\,(96485 \text{ C mol}^{-1})\,(-1.5 \text{ V}) = -289{,}400 \text{ J mol}^{-1}$$

Thermodynamics of Electrochemical Systems

First Law $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$

$\mathrm{d}q$ = heat added to the system

$\mathrm{d}w$ = work done on the system $= \mathrm{d}w_{pV} + \mathbf{d}\boldsymbol{w}_{\mathbf{e}}$

Expansion/Compression Work

$$\mathrm{d}w_{pV} = -p_{\mathrm{external}}\mathrm{d}V$$

Electrical Work (“*New*”!)

Electric charge dQ (in units of Coulomb) is transferred from initial electric potential ϕ_{initial} to final electric potential ϕ_{final}.

electrical work $\mathrm{d}w_{\mathrm{e}} = (\phi_{\mathrm{final}} - \phi_{\mathrm{initial}})\mathrm{d}Q$

Thermodynamics of Electrochemical Systems

Change in the Gibbs energy $G = U + pV - TS$ at fixed temperature and pressure ($p = p_{\mathrm{external}}$):

$$
\begin{aligned}
\mathrm{d}G_{T,p} &= \mathrm{d}(U + pV - TS) \\
&= \mathrm{d}U + \mathrm{d}(pV) - \mathrm{d}(TS) \\
&= \mathrm{d}q + \mathrm{d}w + p\mathrm{d}V - T\mathrm{d}S \\
&= \mathrm{d}q - p\mathrm{d}V + \mathrm{d}w_{\mathrm{e}} + p\mathrm{d}V - T\mathrm{d}S \\
&= \mathrm{d}w_{\mathrm{e}} \cancel{+ \mathrm{d}q} - T\mathrm{d}S
\end{aligned}
$$

[recall $\mathrm{d}q \le T\mathrm{d}S$ (2nd Law)]

important conclusion :

$$\boxed{\mathbf{d}G_{T,p} \le \mathbf{d}w_{\mathrm{e}}}$$

Thermodynamics of Electrochemical Systems

For **reversible** processes at fixed temperature and pressure:

$$\Delta G_{T,p} = w_\mathrm{e}$$

The change in the Gibbs free energy is the electrical work "free" to be done on the surroundings.

Applications:

- Use a spontaneous chemical reaction ($\Delta G_{T,p} < 0$) to do electrical work on the surroundings (batteries and fuel cells)
- Perform electrical work on a system to drive a nonspontaneous chemical reaction (electrolytic cells)
- Use electrical measurements to determine accurate ΔG values (and ΔH, ΔS values by differentiation)

Thermodynamics of Electrochemical Systems

For **reversible** processes at fixed temperature and pressure:

$$\boxed{\Delta G_{T,p} = w_\mathrm{e}}$$

Mathematical, thermodynamical, theoretical, abstract, ZZZzzz …?

Consider just one application: lead-acid car batteries

- $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
- 500 million sold per year, 30 billion dollar value
- cheap, reliable, recycled, every car and truck has one

$\Delta G_{T,p}$ and w_e abstract and theoretical ?

Apply left- and right-hand fingers to the terminals of a car battery. The ***jolt*** you get is directly proportional to $\Delta G_{T,p}$ and w_e !

Section 11.4 Electrochemical Cells

a ***different way*** to do chemistry!

PLAN A **Traditional "*Shake-and-Bake* " Chemistry**

- reactants are brought into ***direct physical contact***
- the reaction proceeds

PLAN B **Electrochemistry**

- reactants being oxidized release electrons into an electrode
- the electrons flow through an external circuit (*e.g.*, a wire)
- the electrons enter another electrode to reduce reactants
- oxidization and reduction occur ***at different locations***

Example The spontaneous chemical reaction

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

PLAN A **Direct Chemical Reaction of Zn(s) and Cu^{2+}(aq)**

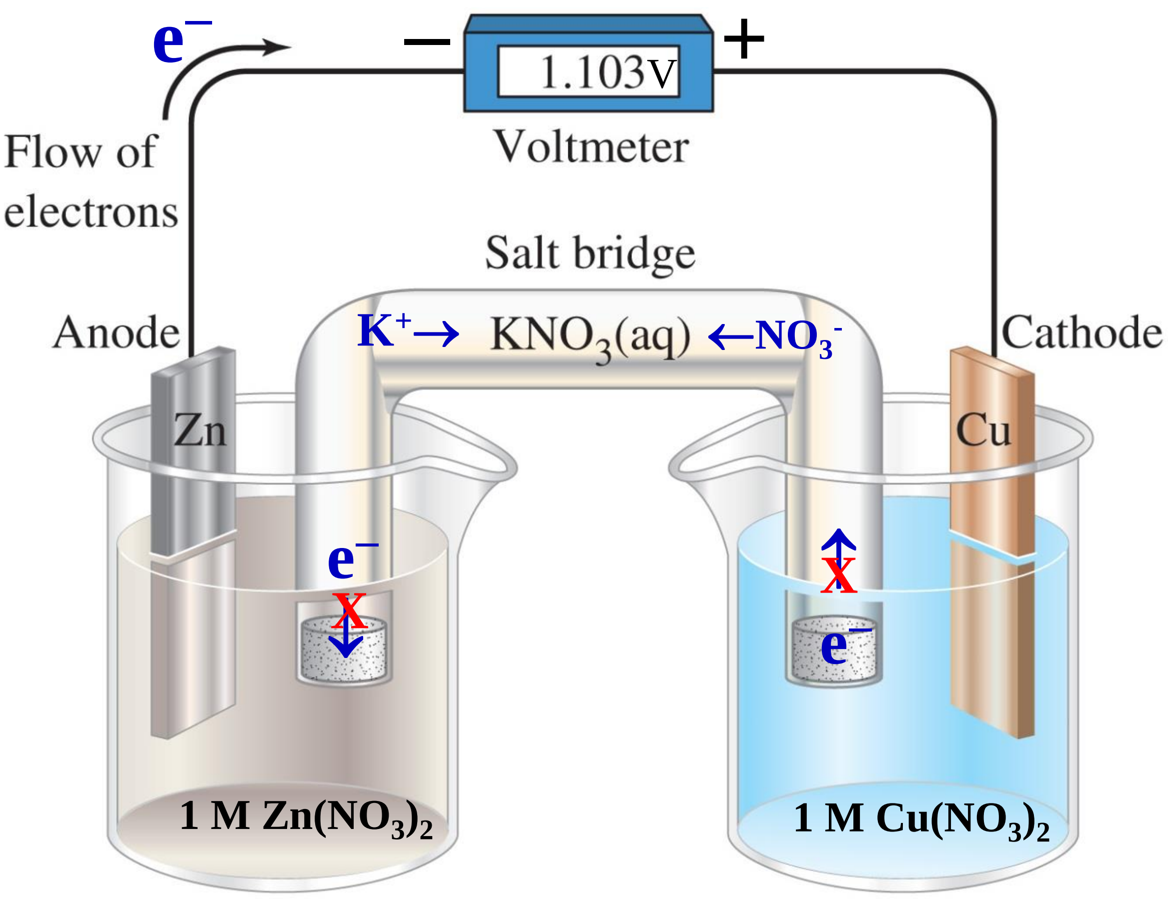
- prepare an aqueous solution of $Cu(NO_3)_2$
- pour the solution of $Cu(NO_3)_2$ onto a sheet of zinc metal
- aqueous Cu^{2+} ions are in physical contact with zinc metal
- zinc metal is oxidized (loses electrons)
- Cu^{2+} ions are reduced (gains electrons)
- deposition of Cu particles turns the zinc surface dark gray

Direct Chemical Reaction of Zn(s) and $Cu^{2+}(aq)$

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

dip a piece of zinc metal in an aqueous copper nitrate solution

PLAN B Electrochemical Reaction of Zn(s) and Cu^{2+}(aq)



OXIDATION

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

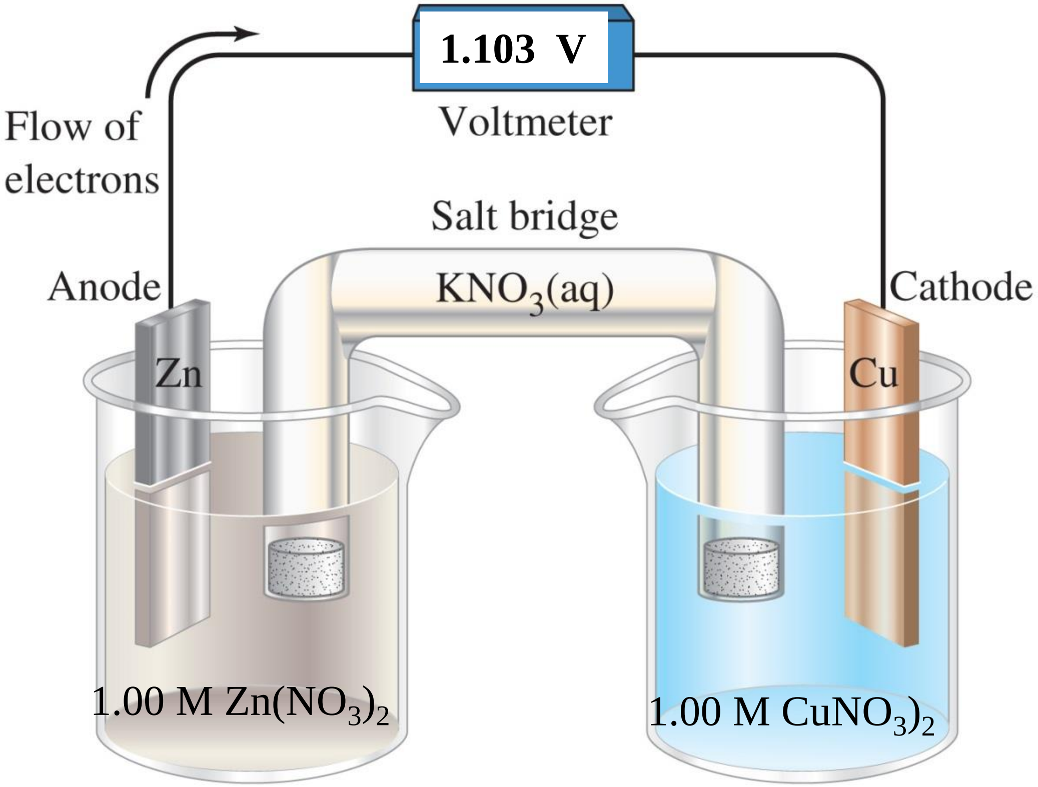
REDUCTION

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

- Zn electrode dipped in $Zn(NO_3)_2$ solution
- Cu electrode dipped in $Cu(NO_3)_2$ solution
- Zn(s) and Cu^{2+}(aq) reactants separated by inert KNO_3 solution
- **electrons flow through the external wire** (not through the solution)
- **ions flow through the electrolyte solutions**

Cell Diagram

Informative, but cumbersome!



left electrode (Ox.)   right electrode (Red.)

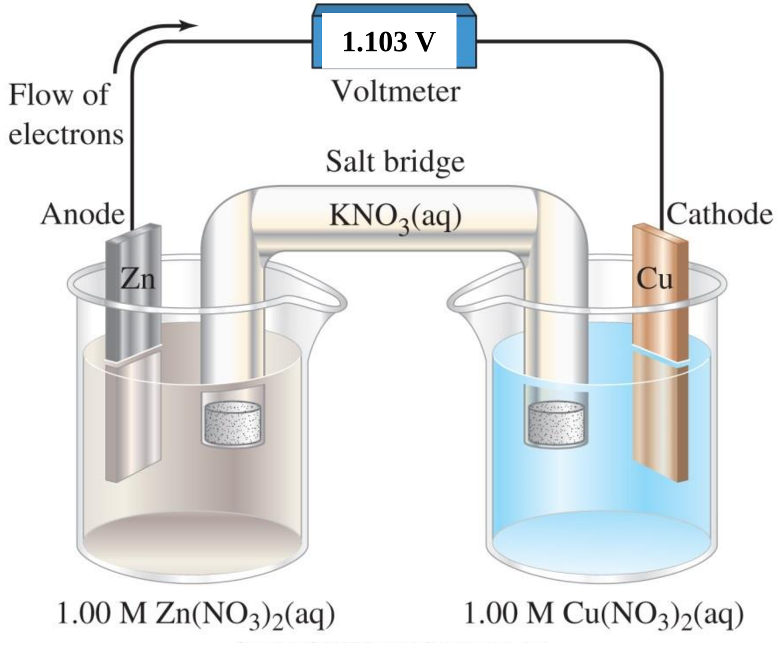
$\mathbf{Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}}$ $\mathbf{Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)}$

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

Electrochemical Cell Notation (concise cell description)

$\mathrm{Zn(s)}\,|\,\mathrm{Zn(NO_3)_2}$ (aq, 1.00 M) $||\,\mathrm{Cu(NO_3)_2}$(aq, 1.00 M) $|\,\mathrm{Cu(s)}$

Describes the cell:



Conventions

left electrode: anode (oxidation)

right electrode: cathode (reduction)

cell potential:
$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$
$$= E_{\text{Cu}} - E_{\text{Zn}}$$
$$= 1.103 \text{ Volt}$$

phase boundary: $|$

salt bridge (or porous barrier): $||$

(prevents mixing of anode and cathode electrolytes)

Example Write the balanced reaction for the cell:

$$\mathrm{Pt(s)|H_2(g,1\ atm)|HCl(aq,\ 0.10\ M)|\ AgCl(s)|Ag(s)}$$

left electrode (anode, oxidation)

$H_2(g)$ hydrogen in oxidation state 0

$H^+(aq)$ hydrogen in oxidation state +1

$$\mathrm{H_2(g) \rightarrow 2H^+(aq) + 2e^-\ (in\ Pt)}$$

L reaction

right electrode (cathode, reduction)

Ag(s) silver in oxidation state 0

AgCl(s) silver in oxidation state +1

$$\mathrm{AgCl(s) + e^-\ (in\ Ag) \rightarrow Ag(s) + Cl^-(aq)}$$

R reaction

balance *the number of electrons* (**L reaction** plus ***twice*** **R reaction**) to get:

$$\mathrm{H_2(g) + 2AgCl(s) \rightarrow 2H^+(aq) + 2Cl^-(aq) + 2Ag(s)}$$

n = 2 moles of electrons flow through the external circuit. Sketch the cell?

Reversible Electrochemical Cell ($\Delta G = w_e$)

Transfer ***n*** moles of electrons (electric charge $-nF$ Coulombs) from the left electrode to right electrode through voltage difference $E = \phi_R - \phi_L$

electrical work = charge × voltage difference

$$\boxed{w_e = -nFE = \Delta G}$$

Faraday constant F = 96,485 coulombs per mole (the charge on one mole of protons)

Cell: $\mathbf{Pt(s)|H_2(g,0.2\ atm)|HCl(aq,\ 0.10\ m)|\ AgCl(s)|Ag(s)}$

Calculate ΔG and the cell voltage E at T = 298 K.

overall cell reaction (transfer two moles of electrons, $n = 2$)

$$\mathbf{H_2(g) + 2AgCl(s) \rightarrow 2H^+(aq) + 2Cl^-(aq) + 2Ag(s)}$$

Gibbs energy change

$$\Delta G = \Delta G^{o} + RT \ln Q$$

standard Gibbs energy change (*all chemicals in their standard states*)

$$\Delta G^{o} = 2\Delta G_{fm}^{o}(H^+,aq) + 2\Delta G_{fm}^{o}(Cl^-,aq) + 2\Delta G_{fm}^{o}(Ag,s) - \Delta G_{fm}^{o}(H_2,g) - 2\Delta G_{fm}^{o}(AgCl,s) = -42.8 \text{ kJ mol}^{-1}$$

(from data Tables)

reaction quotient
(ideal solutions)

$$Q = \frac{(m_{H+})^2\,(m_{Cl-})^2}{p_{H2}} = \frac{0.10^2\ 0.10^2}{0.2} = 0.05$$

Gibbs energy change for the cell reaction

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$$= -42{,}800\ \mathrm{J\ mol^{-1}} + (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(298\ \mathrm{K})\ \ln(0.05)$$

$$= -50{,}220\ \mathrm{J\ mol^{-1}} \qquad (< 0,\ \text{spontaneous cell reaction})$$

cell voltage

[use $\Delta G = -nFE$ to get $E = -\Delta G / (nF)$]

$$E = -\Delta G /(nF)$$

$$= -(-50{,}220\ \mathrm{J\ mol^{-1}}) / (2 \times 96485\ \text{Coulomb mol}^{-1})$$

$$= 0.2603\ \text{volt} \qquad (E > 0,\ \text{spontaneous cell reaction})$$

standard cell voltage

[all chemicals in their standard states]

$$E^{\circ} = -\Delta G^{\circ}/(nF)$$

$$= -(-42{,}800\ \mathrm{J\ mol^{-1}}) / (2 \times 96485\ \text{Coulomb mol}^{-1})$$

$$= 0.2218\ \text{volt}$$

Nernst Equation. *Used to Predict Cell Voltages*

$\Delta G = \Delta G^{o} + RT \ln Q$ divide by $-nF$

$$\frac{\Delta G}{-nF} = \frac{\Delta G^{o}}{-nF} + \frac{RT}{-nF} \ln Q$$

$$E = E^{o} - \frac{RT}{nF} \ln Q$$ **Nernst equation**

E	cell voltage ($E = -\Delta G / nF$)
E^{o}	standard cell voltage, reactants and products in their standard states ($E^{o} = -\Delta G^{o} / nF$)
Q	reaction quotient
n	number of moles of electrons transferred

$$E = E^{o} - \frac{RT}{nF}\ln Q$$ **Nernst equation**

cell voltage $E = -\Delta G / nF$

spontaneous cell reaction:

$E > 0$ $\Delta G < 0$ $Q < K$ (reaction equilibrium constant)

non-spontaneous cell reaction:

$E < 0$ $\Delta G > 0$ $Q > K$

at equilibrium:

$E = 0$ $\Delta G = 0$ $Q = K$

$0 = E^{o} - (RT/nF)\ln K$ so $\ln K = nFE^{o}/RT$

$= -\Delta G^{o}/RT$

Write the **Nernst equation** for the reversible cell:

Pt(s)|H_2(g, 0.2 atm)|HCl(aq, 0.10 m)| AgCl(s)|Ag(s)

with the reaction

$$\mathbf{H_2(g) + 2AgCl(s) \rightarrow 2H^+(aq) + 2Cl^-(aq) + 2Ag(s)}$$

$n = 2$ (two moles of electrons transferred),
reaction quotient (assuming ideal solutions):

$$Q = \frac{(a_{H+})^2(a_{Cl-})^2}{p_{H2}} = \frac{(\gamma_{H+}m_{H+})^2(\gamma_{Cl-}m_{Cl-})^2}{p_{H2}} \approx \frac{(m_{H+})^2(m_{Cl-})^2}{p_{H2}}$$

Nernst equation $E = E^{o} - \dfrac{RT}{2F} \ln \dfrac{m_{H+}{}^2\, m_{Cl-}{}^2}{p_{H2}}$

For this cell, use $m_{H+} = m_{Cl-} = 0.10$ mol kg^{-1} and $p_{H2} = 0.2$ atm.

!! Warning !!

A) The Nernst equation is exact only for reversible cells:

- no irreversible mixing (*e.g.*, no salt bridges or porous barriers)
- no side reactions
- electrode kinetics fast enough to transfer electrons

B) For accurate calculations, **ionic activities** a_i should be used instead of ionic molalities to allow for nonideal solution behavior.

For example:

$$a_{\mathrm{H^+}} = \gamma_{\mathrm{H^+}} m_{\mathrm{H^+}}$$

$$a_{\mathrm{Cl^-}} = \gamma_{\mathrm{Cl^-}} m_{\mathrm{Cl^-}}$$

$$a_{\mathrm{HCl}} = a_{\mathrm{H^+}} a_{\mathrm{Cl^-}} = \gamma_{\pm}^2 m_{\mathrm{HCl}}^2$$

Example Nonideal Nernst equation for the reversible cell:

$$\mathbf{Pt(s)|H_2(g,\ 0.2\ bar)|HCl(aq,\ \mathit{m} = 0.10\ mol\ kg^{-1})|\ AgCl(s)|Ag(s)}$$

with the reaction

$$\mathbf{H_2(g) + 2AgCl(s) \rightarrow 2H^+(aq) + 2Cl^-(aq) + 2Ag(s)}$$

$n = 2$ (two moles of electrons transferred) and $m_{\mathrm{H+}} = m_{\mathrm{Cl-}} = m$

$$Q = \frac{(a_{\mathrm{H+}})^2 (a_{\mathrm{Cl-}})^2}{p_{\mathrm{H2}}} = \frac{(\gamma_{\mathrm{H+}})^2 (\gamma_{\mathrm{Cl-}})^2 m^4}{p_{\mathrm{H2}}} = \frac{(\gamma_{\pm})^4 m^4}{p_{\mathrm{H2}}}$$

Nernst equation $E = E^{\circ} - \dfrac{RT}{2F} \ln \dfrac{(\gamma_{\pm})^4 m^4}{p_{\mathrm{H2}}}$

Possibilities?

For this cell: $m_{\mathrm{H+}} = m_{\mathrm{Cl-}} = m = 0.10$ mol kg^{-1}, $\gamma_{\pm} = 0.796$ and $p_{\mathrm{H2}} = 0.2$ bar

Section 11.5 Standard Electrode Potentials

Electrochemical cell voltages E are <u>differences</u> in electric potential between the anode and cathode electrodes

$$\begin{aligned} E &\equiv E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{right}} - E_{\text{left}} \quad \text{(conventional cell notation)} \end{aligned}$$

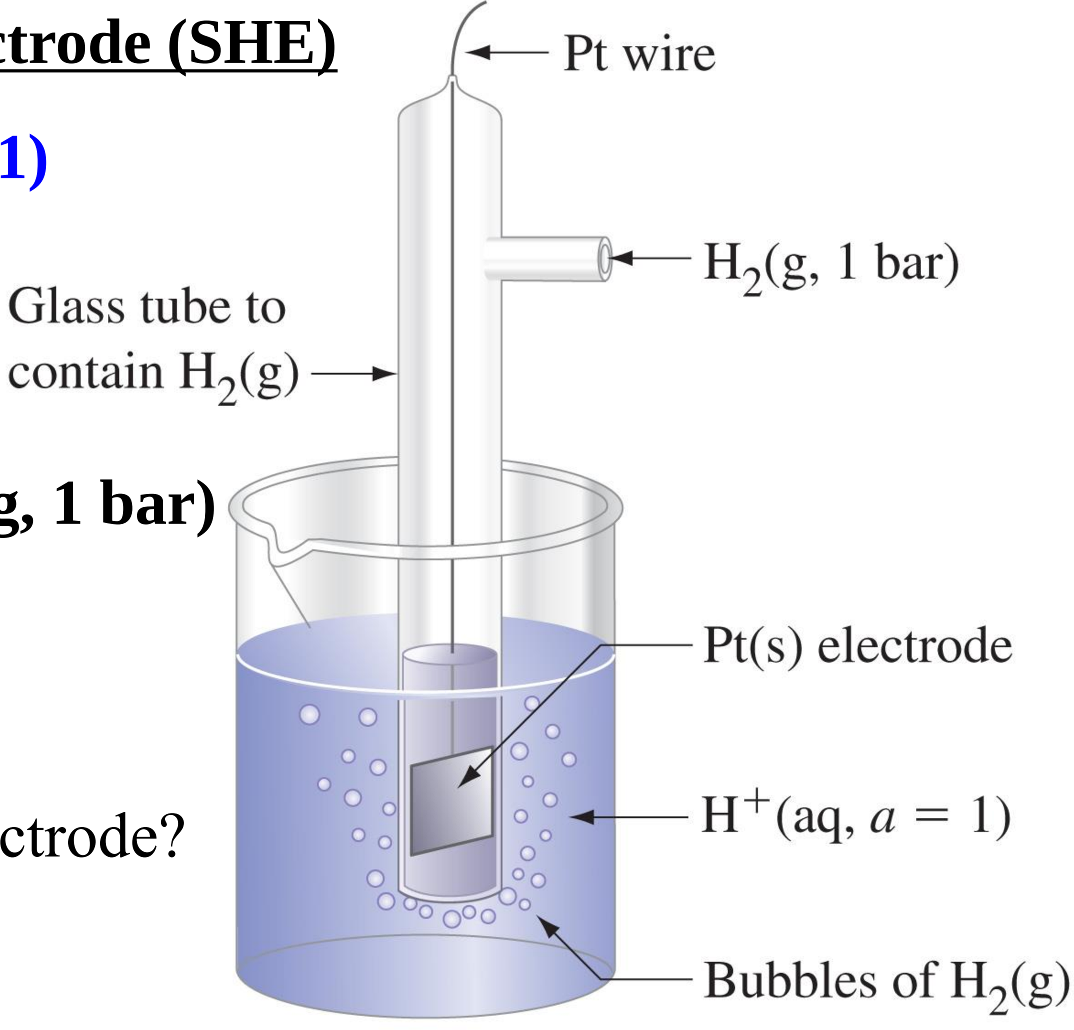
The electric potential of an individual electrode cannot be measured

Standard Hydrogen Electrode (SHE)

For convenient calculation of cell voltages, the electric potential of the **standard hydrogen electrode (SHE)**

$\mathbf{Pt|H_2(g,\ 1\ bar)|H^+(}\boldsymbol{a}_{\mathbf{H+}}\mathbf{\ =\ 1)}$

is **defined as zero volts**.



$$\mathbf{2H^+(aq,\ }\boldsymbol{a}_{\mathbf{H+}}\mathbf{\ =\ 1)\ +\ 2e^-\ \ =\ \ H_2(g,\ 1\ bar)}$$

$$\boldsymbol{E}^{\,\mathbf{o}} \equiv \mathbf{0\ V\ (exact)}$$

Why “standard” hydrogen electrode?

H^+ and H_2 are at unit activity.

The standard hydrogen electrode is used to determine the standard potentials of other electrodes. *Example*:

$\mathbf{Pt|H_2(g,\ 1\ bar)|H^+(\mathit{a}_{H+} = 1)\ ||\ Cu^{2+}(\mathit{a}_{Cu2+} = 1)|Cu(s)}$ $E^{o}_{\text{cell}} = 0.340\text{ V}$

anode **cathode**

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

Standard cell potential: the potential difference of a cell formed from two *standard* electrodes.

$$E^{o}_{\text{cell}} = 0.340\text{ V} = E^{o}_{\text{cathode}} - E^{o}_{\text{anode}} = E^{o}_{\text{Cu2+/Cu}} - 0$$

$$\mathbf{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad \mathit{E}^{o}_{Cu^{2+}/Cu} = 0.340\ V}$$

a standard reduction potential

Standard Reduction Potentials are used to Calculate Standard Cell Voltages ($E^{\,o}$)

Example: Determine $E^{\,o}$ for the zinc-chlorine battery at 25 °C.

$\mathbf{Zn(s)|ZnCl_2(aq)|Cl_2(g)|Pt(s)}$ $E^{\,o}_{\mathrm{cell}} = ?$

Anode: $\mathbf{Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-}$ $E^{o}_{\mathrm{anode}} = -E^{o}_{\mathrm{Zn2+/Zn}}$

Cathode: $\mathbf{Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)}$ $E^{o}_{\mathrm{cathode}} = E^{o}_{\mathrm{Cl2/Cl-}}$

Overall: $\mathbf{Zn(s) + Cl_2(g) \rightarrow ZnCl_2(aq)}$ $E^{o}_{\mathrm{cell}} = E^{o}_{\mathrm{anode}} + E^{o}_{\mathrm{cathode}}$

The standard potential for the cathode (reduction) is the standard reduction potential $E^{\,o}_{\mathrm{Cl2/Cl-}} = 1.358$ V for chlorine.

The anode (oxidation) standard potential $E^{\,o}_{\mathrm{Zn/Zn2+}}$ is obtained by **reversing** the $Zn^{2+}(aq)$ standard reduction reaction:

$$E^{\,o}_{\mathrm{Zn/Zn2+}}\ (\mathrm{ox.}) = -E^{\,o}_{\mathrm{Zn2+/Zn}}\ (\mathrm{red.}) = -(-0.763)\ \mathrm{V}$$

Cathode The standard potential for the cathode (reduction) is the standard reduction potential for Cl_2.

$$\mathbf{Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)} \qquad E^o_{\mathrm{cathode}} = E^o_{\mathrm{Cl2/Cl-}} = 1.358\ \mathrm{V}$$

Anode The standard potential for the anode (oxidation) is obtained by reversing the $Zn^{2+}(aq)$ reduction reaction

$$\mathbf{Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)} \qquad E^o_{\mathrm{Zn2+/Zn}} = -0.763\ \mathrm{V}$$

to give the standard anode potential +0.763 V for the oxidation

$$\mathbf{Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-} \qquad E^o_{\mathrm{anode}} = -E^o_{\mathrm{Zn2+/Zn}} = -(-0.763\ \mathrm{V})$$

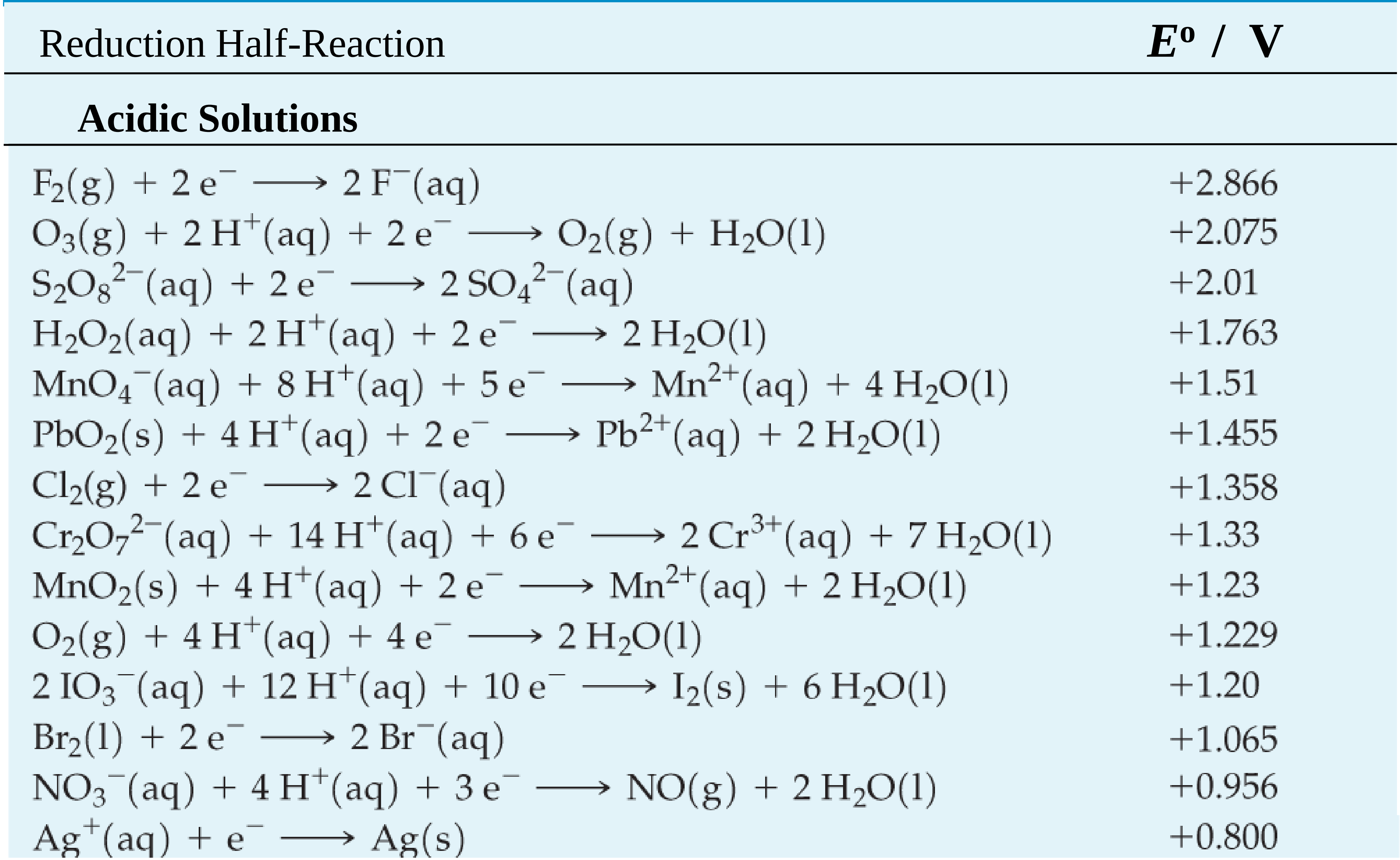
Overall Cell Reaction

$$\mathbf{Zn(s) + Cl_2(g) \rightarrow ZnCl_2(aq)} \qquad E^o_{\mathrm{cell}} = E^o_{\mathrm{anode}} + E^o_{\mathrm{cathode}}$$

$$= 1.358\ \mathrm{V} + 0.763\ \mathrm{V}$$

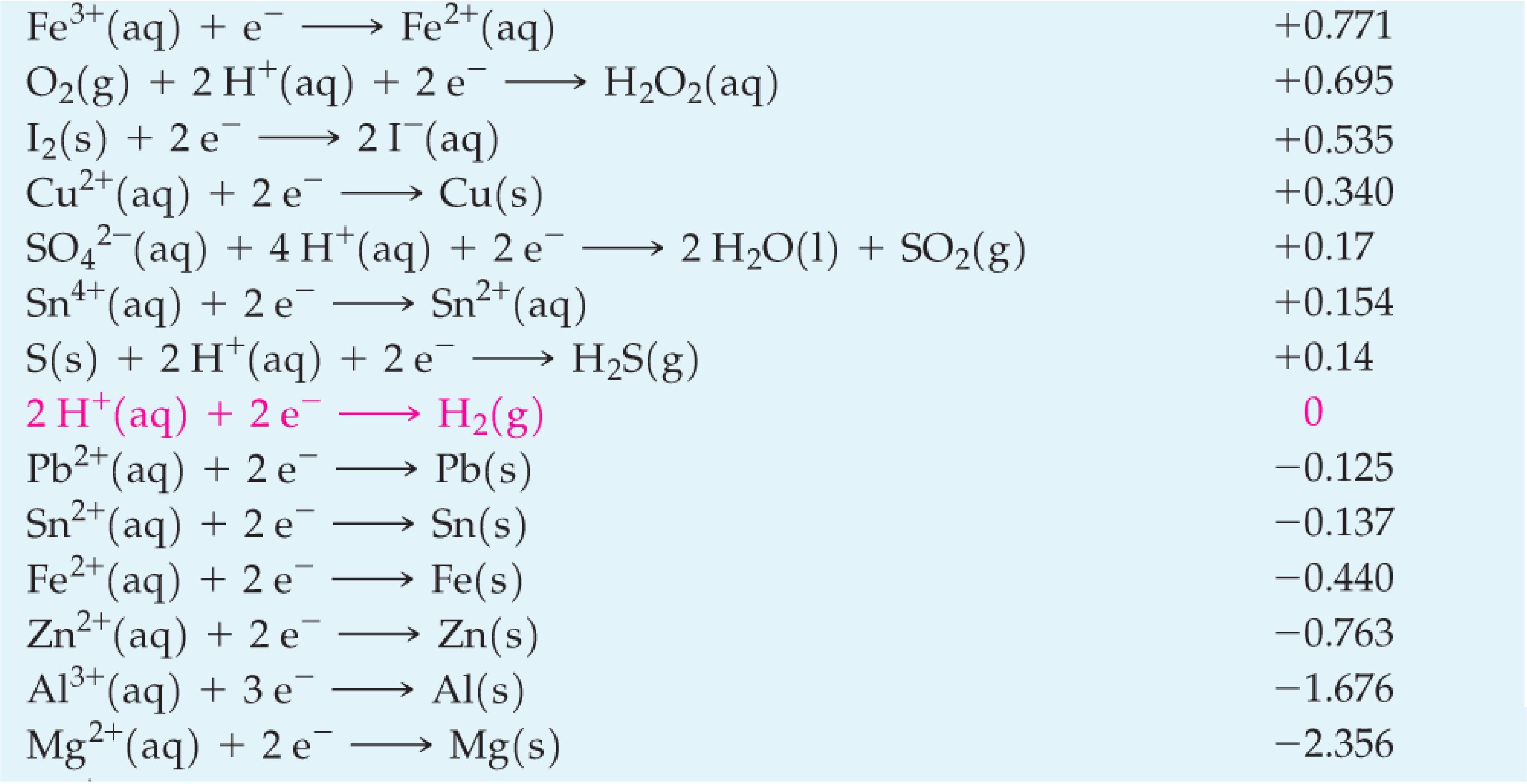
$$= \mathbf{2.121\ V}$$

Standard Reduction Potentials at 25° C



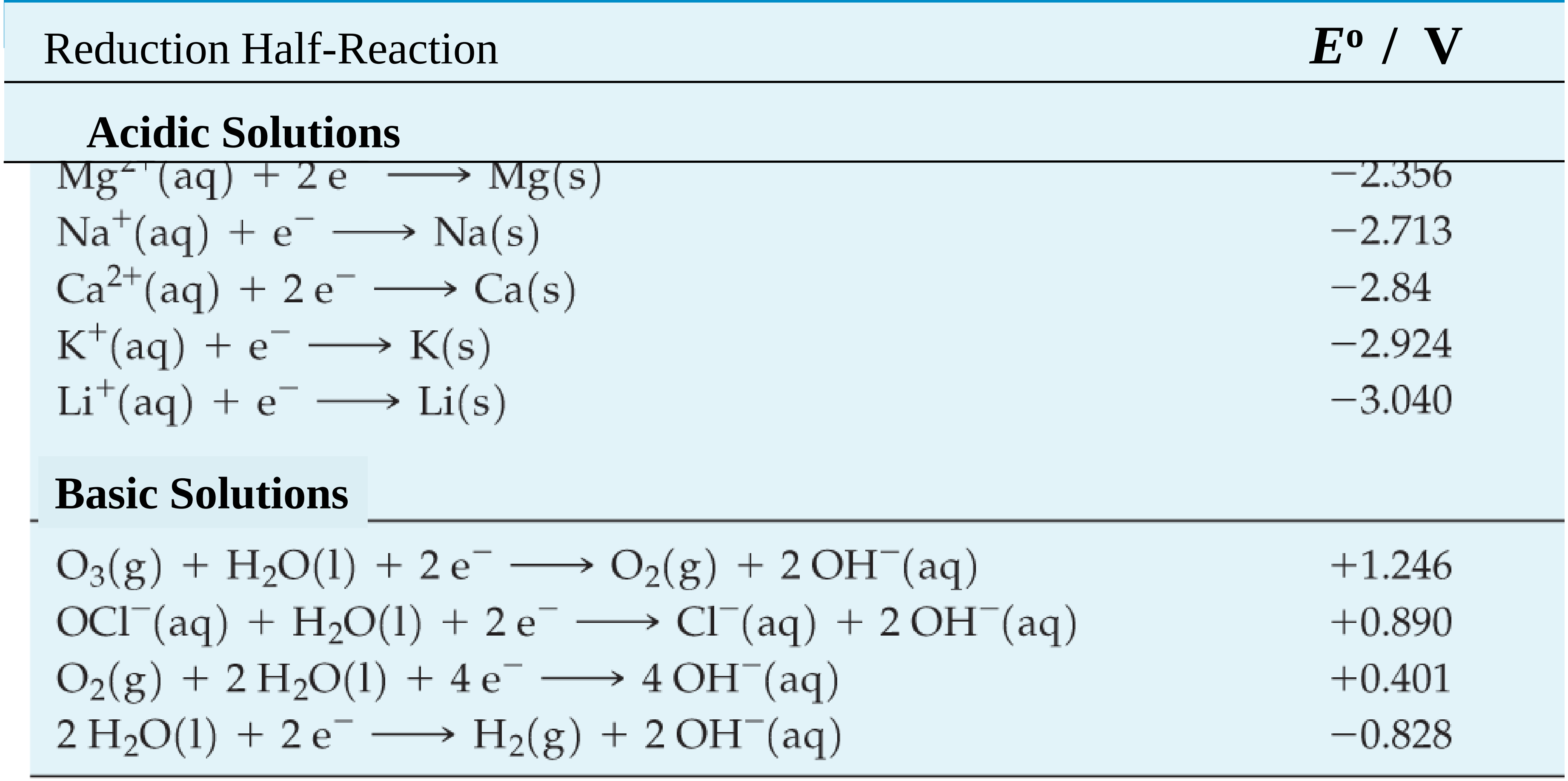
Reduction Half-Reaction	E^o / V
Acidic Solutions	
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.866
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O(l)$	+2.075
$S_2O_8^{2-}(aq) + 2e^- \longrightarrow 2SO_4^{2-}(aq)$	+2.01
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$	+1.763
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$	+1.455
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.358
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.229
$2IO_3^-(aq) + 12H^+(aq) + 10e^- \longrightarrow I_2(s) + 6H_2O(l)$	+1.20
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.065
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$	+0.956
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.800

Standard Reduction Potentials at 25° C



Reduction Half-Reaction	E^o / V
Acidic Solutions	
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$	+0.695
$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$	+0.535
$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$	+0.340
$SO_4{}^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \longrightarrow 2\,H_2O(l) + SO_2(g)$	+0.17
$Sn^{4+}(aq) + 2\,e^- \longrightarrow Sn^{2+}(aq)$	+0.154
$S(s) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2S(g)$	+0.14
$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$	−0.125
$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$	−0.137
$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	−0.440
$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	−0.763
$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	−1.676
$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$	−2.356

Standard Reduction Potentials at 25° C



Reduction Half-Reaction	**E^o / V**
Acidic Solutions	
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.356
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.713
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.84
$K^+(aq) + e^- \longrightarrow K(s)$	−2.924
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.040
Basic Solutions	
$O_3(g) + H_2O(l) + 2e^- \longrightarrow O_2(g) + 2OH^-(aq)$	+1.246
$OCl^-(aq) + H_2O(l) + 2e^- \longrightarrow Cl^-(aq) + 2OH^-(aq)$	+0.890
$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$	+0.401
$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.828

Sections 11.6 to 11.8 Thermodynamic Data from Electrochemical Cells

Example Use measured voltages to determine the standard cell potential and activity coefficients for the reversible cell:

$$\mathbf{Pt(s)|H_2(g,\ \boldsymbol{p}^o = 1\ bar)|HCl(aq,\ 0.10\ m)|\ AgCl(s)|Ag(s)}$$

with $a_{H2} = 1$ and the reaction ($n = 2$ moles of electrons transferred)

$$\mathbf{H_2(g) + 2AgCl(s) \rightarrow 2H^+(aq) + 2Cl^-(aq) + 2Ag(s)}$$

$$\boxed{E = E^o - \frac{RT}{2F}\ln(\gamma_\pm^2 m^2)^2 = E^o - \frac{2RT}{F}\ln(\gamma_\pm m)}$$

Measure E. But there are two unknowns: E^o and $\gamma_\pm$!

No problem! Rearrange the Nernst equation:

$$\boxed{E + \frac{2RT}{F}\ln m = E^{\mathrm{o}} - \frac{2RT}{F}\ln\gamma_{\pm}}$$

1) Measure cell voltage *E* for different HCl molalities *m*.

2) Plot $E + (2RT/F)\ln m$ against $m^{1/2}$. **(Why square-root *m*?)**

3) Calculate the intercept $= E^{\mathrm{o}}$

4) Once the standard cell voltage E^{o} is known, the mean ionic activity coefficient $\gamma_{\pm}$ can be calculated for each HCl solution.

ΔG, ΔS, ΔH, ΔV from Electrochemical Cell Data

1) Measure cell voltage E. Calculate $\boldsymbol{\Delta G = -nFE}$. Easy!

2) Measure cell voltage E at different temperatures at fixed pressure.

Use $\Delta G = -nFE$ and $(\partial \Delta G/\partial T)_p = -\Delta S$ to calculate

$$\boldsymbol{\Delta S = nF\,(\partial E/\partial T)_p}$$ **(no dq_{rev} or calorimetry!)**

3) Once ΔG and ΔS are known, use $\Delta G = \Delta H - T\Delta S$ to calculate

$$\boldsymbol{\Delta H = \Delta G + T\Delta S}$$ **(no calorimetry !)**

Or use $\Delta H = [\partial(\Delta G/T)/\partial(1/T)]_p = -nF\,[\partial(E/T)/\partial(1/T)]_p$

4) Measure cell voltage E at different pressures at fixed temperature.

Use $\Delta G = -nFE$ and $(\partial \Delta G/\partial p)_T = \Delta V$ to calculate

$$\boldsymbol{\Delta V = -nF\,(\partial E/\partial p)_T}$$ **(no density measurements !)**

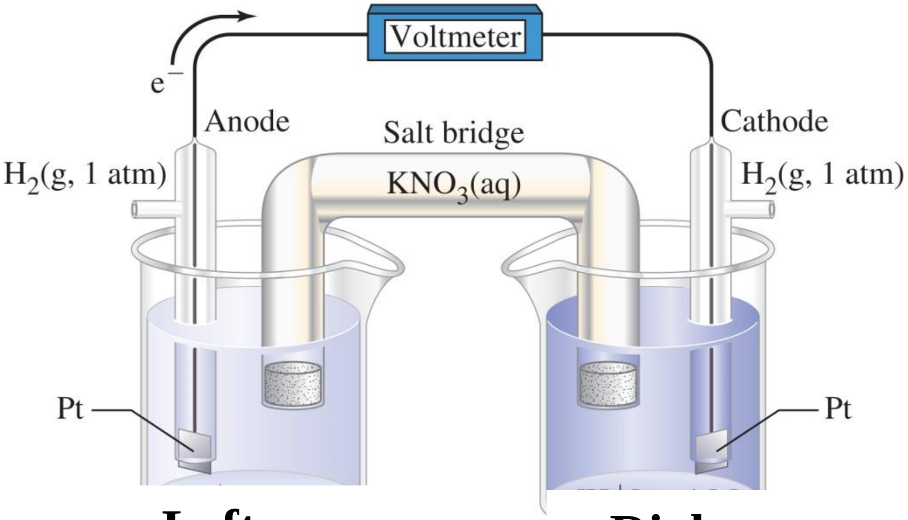
Section 11.9 Electrochemical Cell Terminology

(summary)

Anode	Electrode where **oxidation** occurs
Cathode	Electrode where **reduction** occurs
Galvanic Cell	Voltage produced by **spontaneous chemical reaction**
Cell Potential *E*	Cathode voltage minus anode voltage
Electrolytic Cell	Applied voltage used to drive **non-spontaneous reaction**
Concentration Cell	Identical electrodes, but **different ion concentrations**
Electrolyte Solution	Conducts electricity by the **movement of ions** (not electrons)
External Circuit (Metal Wire)	Conducts electricity by the **movement of electrons**

Concentration Cells: ***Identical electrodes*** but different ion concentrations. **Example:**

$$\mathbf{Pt(s)|H_2\ (1\ atm)|H^+(aq,\ \mathit{a}_{H+(reference)})||H^+(aq,\ \mathit{a}_{H+}?)|H_2(1\ atm)|Pt(s)}$$



Left

$$\boldsymbol{a}_{\mathbf{H+(reference)}}$$

Right

$$\boldsymbol{a}_{\mathbf{H+}} = ?$$

$$\mathbf{H_2(g,\ 1\ atm) \rightarrow 2\ H^+(\mathit{a}_{H+(reference)}) + 2\ e^-}$$

$$\mathbf{2\ H^+(a_{H+}?) + 2e^- \rightarrow 2\ H_2(g,\ 1\ atm)}$$

$$\mathbf{2\ H^+(\mathit{a}_{H+}?) \rightarrow 2\ H^+(\mathit{a}_{H+(reference)})}$$

$$\begin{aligned}\Delta G^{o} &= \Delta G_f^{o}(\text{products}) - \Delta G_f^{o}(\text{reactants}) \\ &= \Delta G_f^{o}(\text{H}^+,\text{aq}) - \Delta G_f^{o}(\text{H}^+,\text{aq}) = 0\end{aligned}$$

$$\boldsymbol{E^{o} = -\Delta G^{o}/2F = 0}$$

$$E = = \overset{0}{\cancel{E^{o}}} - (RT/2F)\ln(a_{\text{H+right}}{}^2/\text{a}_{\text{H+left}}{}^2) = (RT/F)\ln(\text{a}_{\text{H+}}?/1)$$

$$\boxed{E = -(RT/F)\ln[\,a_{\text{H+}}?/a_{\text{H+(reference)}}\,]}$$

Glass Electrode: Electrochemical pH Measurement

Use silver/silver chloride electrodes to measure the potential difference across a glass membrane permeable to H^+ ions (**H^+ concentration cell**).

$\mathrm{Ag|AgCl(s)|Cl^-(1.0M),H^+(ref.}\ a_{H+})\ |$ glass membrane $|\ \mathrm{H^+}(a_{H+})||\ \mathrm{Cl^-(1.0\ M)|AgCl(s)|Ag(s)}$

$$\mathrm{Ag(s)} + \mathrm{Cl^-\,(1.0\ M)} \rightarrow \mathrm{AgCl(s)} + e^-$$
$$\mathrm{H^+}\ \text{(reference activity)} \rightarrow \mathrm{H^+}\ \text{(unknown activity)}$$
$$\mathrm{AgCl(s)} + e^- \rightarrow \mathrm{Ag(s)} + \mathrm{Cl^-\,(1.0\ M)}$$

Cell Reaction: **H^+ (reference activity)** → **H^+ (unknown activity)**

$$\mathrm{pH} \equiv -\log_{10} a_{H+} = -\log_{10}(\gamma_{H+} m_{H+})$$

Important: a_{H+} and γ_{H+} *can't be measured!*

Glass Electrode: Electrochemical pH Measurement

H^+ (reference activity) → H^+ (unknown activity X)

Nernst Equation (use $\log_{10} a = \ln a / 2.303$):

$$E = -(RT/F)\ln(a_{\mathrm{H+}X} / a_{\mathrm{H+ref}})$$

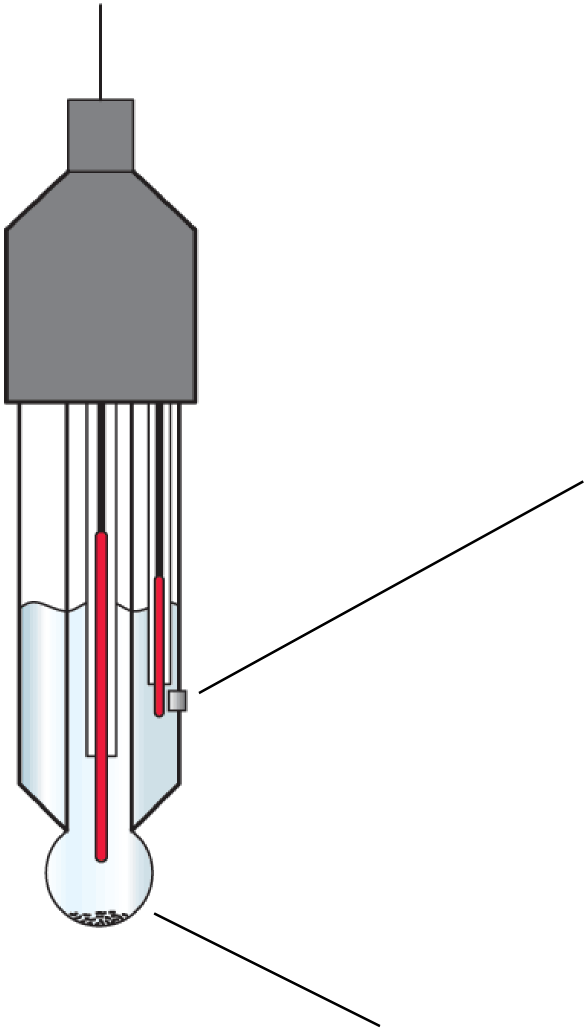
$$FE/RT = -\ln a_{\mathrm{H+}X} + \ln a_{\mathrm{H+ref}}$$

$$FE/(RT\ln 10) = -\ln a_{\mathrm{H+}} / \ln 10 + \ln a_{\mathrm{H+ref}}/\ln 10$$

$$FE/(RT\ln 10) = \mathrm{pH}_X - \mathrm{pH}_{\mathrm{ref}}$$

In practice, use a buffer solution with a known pH (close to the unknown pH_X) as the reference solution.

“Combination pH” Electrode



Ag/AgCl electrodes (**red**) on opposite sides of a glass electrode (the bulb).

A small porous disc on the side of the outer glass tube acts as a salt bridge.

The porous disc connects the (right) Ag/AgCl electrode with the solution in which the pH electrode is dipped.

glass membrane permeable to H^+ ions

Ion Selective Electrodes: Electroanalytical Chemistry

Ion^{Z+} (reference activity) → Ion^{Z+} (unknown activity X)

Commercially available electrodes are used to measure the activities and concentrations of many important species:

H^+

Na^+

K^+

Ca^{2+}

Cl^-

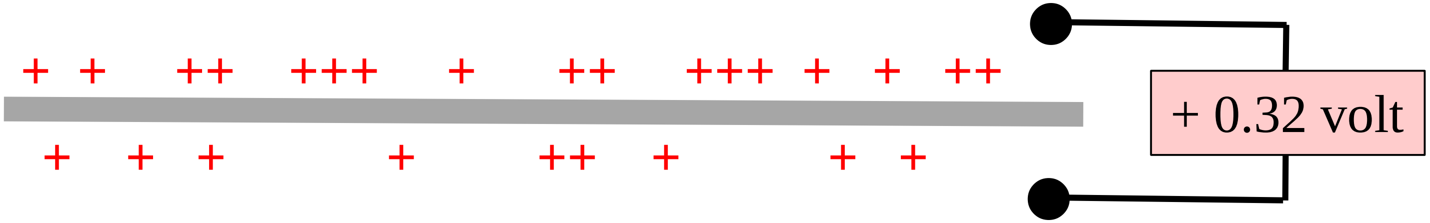
F^-

NO_3^- *etc.*

Electrochemical measurements:

- versatile
- relatively cheap
- reliable (no moving parts),
- highly sensitive (ppb or below)
- easily automated
- no labor required

also … Biological Membrane Potentials



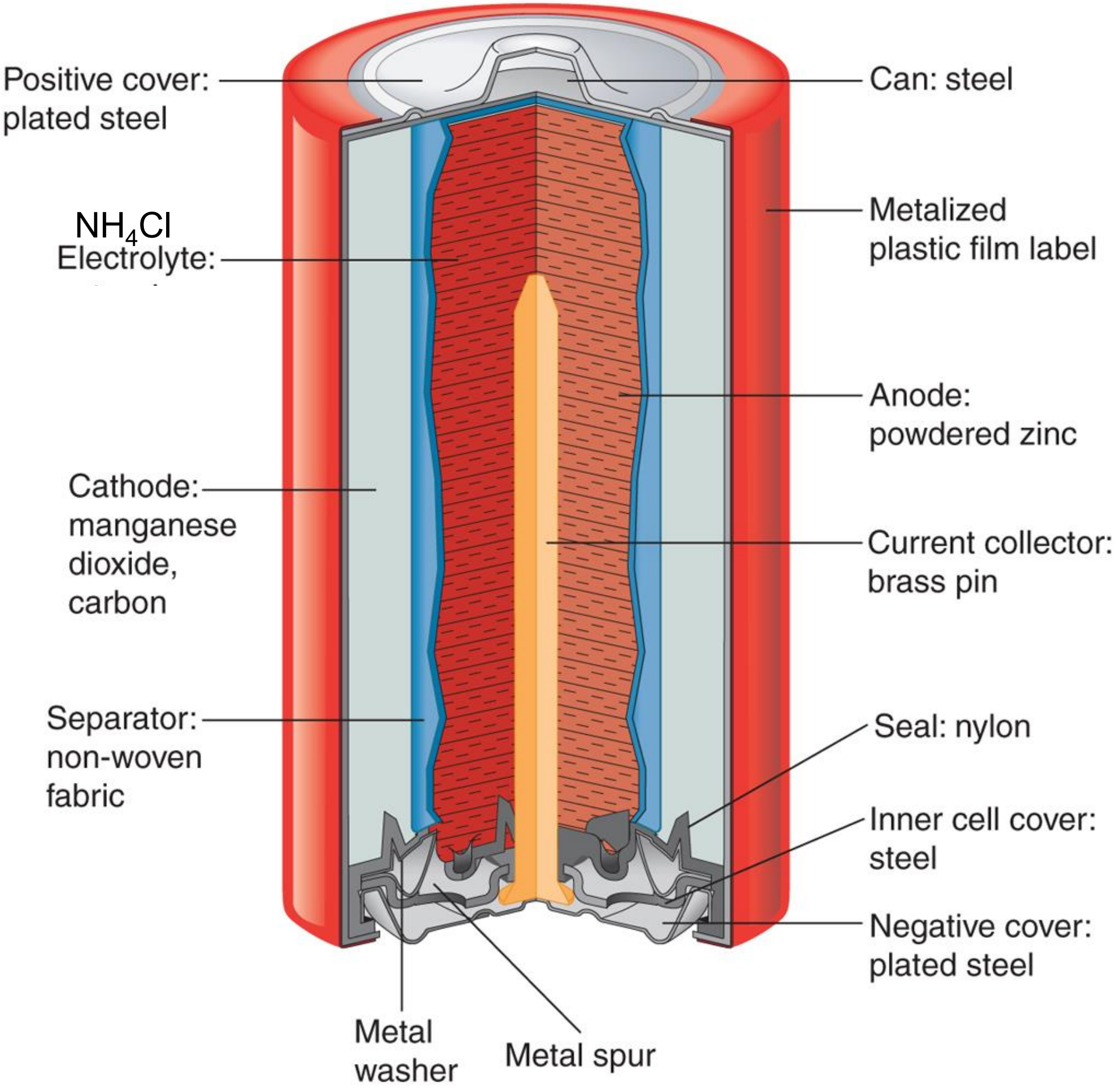
- different ion concentrations on opposite sides of semi-permeable biological membranes generate voltage differences ***without electrodes***
- biological membrane potentials generate nerve impulses
- nerve impulses can be regulated by changing membrane permeability to different ions

Sections 11.11 to 11.13 Electrochemical Devices

Primary Batteries:	• Not rechargeable • Cell reaction not reversible.
Secondary Batteries:	• Rechargeable • Cell reaction can be reversed by passing electricity through the cell
Fuel Cells:	• Fresh reactants continuously fed into the anode and cathode cell compartments
Electrolytic Cells:	• Applied cell voltage drives a nonspontaneous reaction

Leclanche Dry Cell

$E \approx 1.5$ V



- cheap
- non-toxic
- disposable
- primary cell (not rechargeable)
- about 10 billion sold per year
- **why “*dry*”?**

Leclanche Cell Reactions

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

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

Overall: $Zn(s) + 2\ MnO_2(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2OH^-$

Side reaction: The zinc anode slowly dissolves in the slightly acidic ammonium chloride paste, limiting the shelf-life of the cell.

Alkaline Dry Cells

Replace the NH_4Cl electrolyte in traditional Leclanche dry cells with aqueous KOH or NaOH.

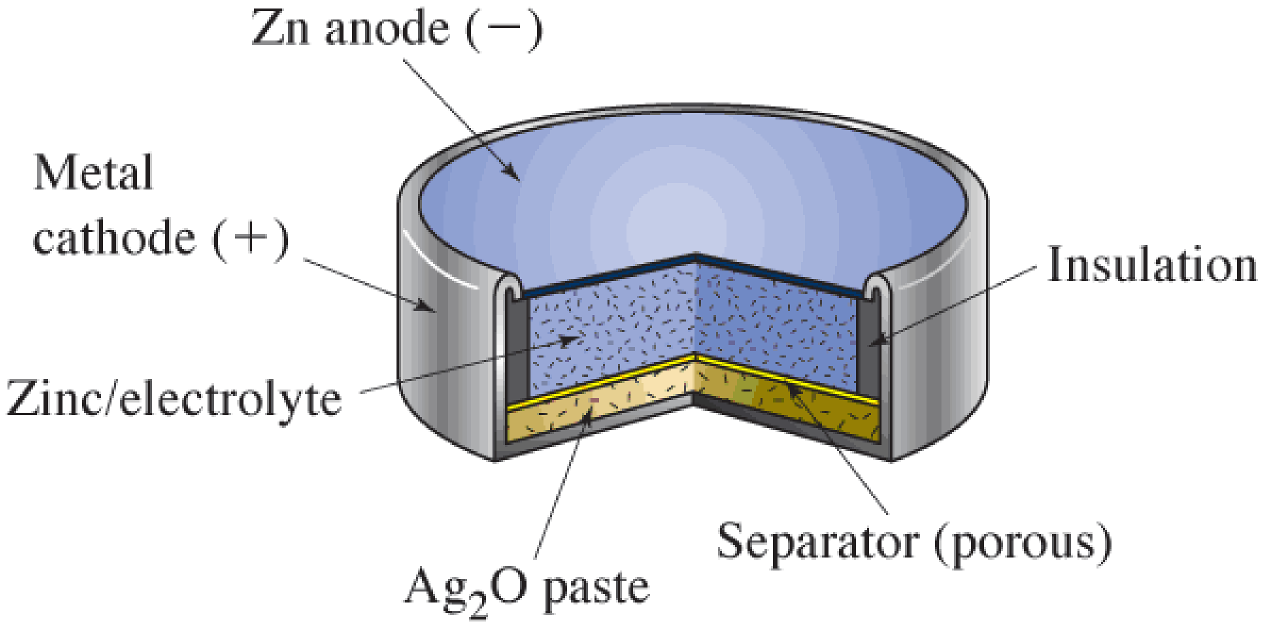
Oxidation : $Zn(s) + 2\ OH^-(aq) \rightarrow Zn\ (OH)_2(s) + 2\ e^-$

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

Overall: $Zn(s) + 2\ MnO_2(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + Mn_2O_3(s)$

Zinc dissolves more slowly in alkaline electrolytes (longer battery shelf-life).

Silver-Zinc “Button” Batteries (1.8 V)



- relatively expensive, *but* …
- high energy density
- suitable for miniature devices (watches, calculators)
- stable cell voltage
- good for critical applications (heart pacemakers, spacecraft)

Silver-Zinc Battery Reactions (*E*° 1.8 V)

$\mathrm{Zn(s)\,|\,ZnO(s)\,|\,KOH(aq)\,|\,Ag_2O(s)\,|\,Ag(s)}$

Oxidation: $\mathrm{Zn(s) + 2\,OH^-(aq) \rightarrow ZnO(s) + H_2O(\mathit{l}) + 2\,e^-}$

Reduction: $\mathrm{Ag_2O(s) + H_2O(\mathit{l}) + 2\,e^- \rightarrow 2Ag(s) + 2\,OH^-(aq)}$

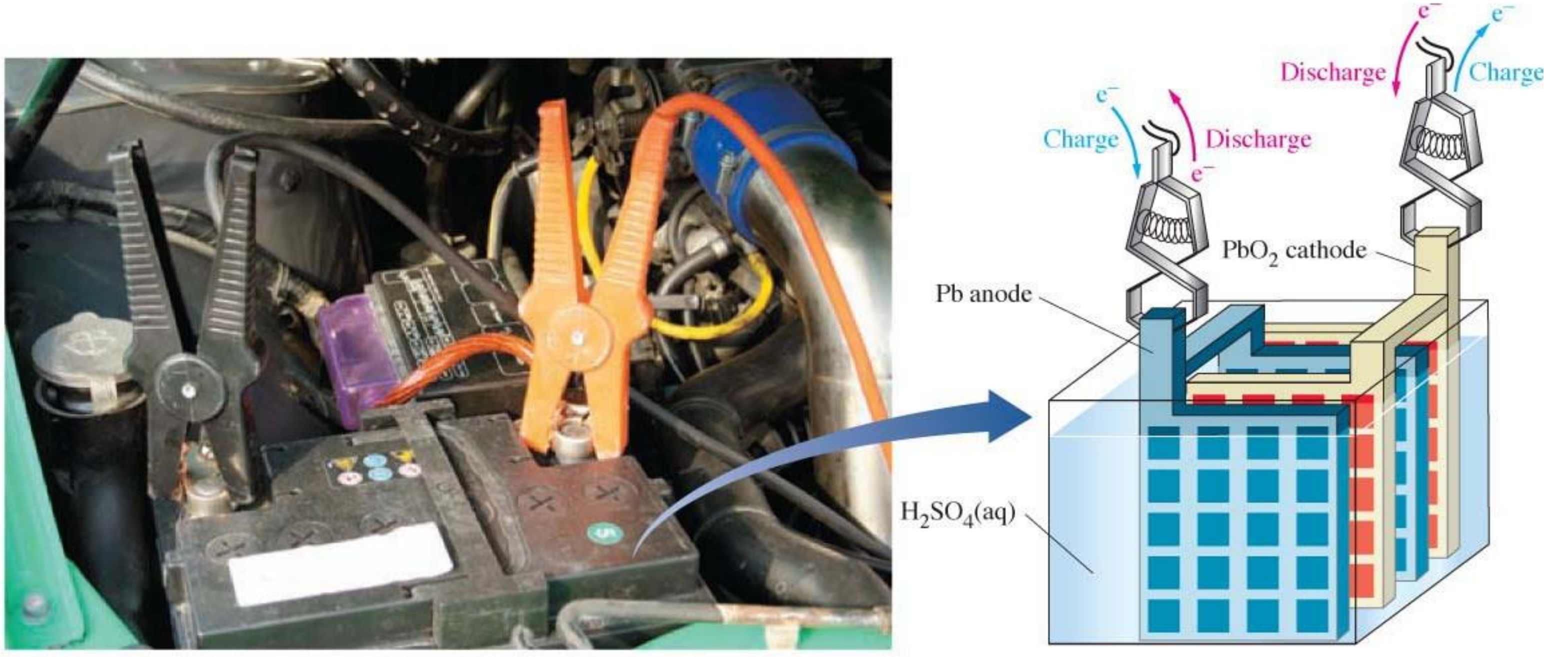
Overall: $\mathrm{Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2\,Ag(s)}$

Voltages of most batteries decrease slightly as they discharge.

Why is the silver-zinc battery voltage constant?

Why does $E = E^{\mathrm{o}}$ for this cell?

Lead-Acid (Storage) Battery (*E* ≈ 2.05 V)



- old technology (but reliable)
- cheap
- contains toxic lead and sulfuric acid (can be recycled)
- heavy (low energy density, unsuitable for miniaturization)
- rechargeable (secondary cell)
- can deliver high pulse currents (≈ 400 amps) for engine ignition

(*what is an amp* (*short for ampere*) ?)

Lead-Acid Battery Reactions

Oxidation:

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

Reduction:

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

Overall:

$$PbO_2(s) + Pb(s) + 2\,H^{+}(aq) + 2HSO_4^{-}(aq) \rightarrow 2\,PbSO_4(s) + 2\,H_2O(l)$$

$$\boxed{E^{o}_{cell} = E^{o}_{PbO_2/PbSO_4} - E^{o}_{PbSO_4/Pb} = 1.74\text{ V} - (-0.28\text{ V}) = 2.02\text{ V}}$$

What are the *oxidation states* of lead in PbO_2, $PbSO_4$, and Pb?

If $\underline{E \approx 2.0\text{ V}}$, then why are automobile lead-acid batteries rated at $\underline{12\text{ V}}$?

Why does the density of the aqueous sulfuric acid electrolyte decrease as the battery discharges? (*A useful battery diagnostic test.*)

Lithium Ion Batteries (*E* ≈ 3.0 V)

Oxidation:

$$\mathrm{LiCoO_2(s)} \rightarrow \mathrm{Li_{1-\mathit{x}}CoO_2(s)} + x\,\mathrm{Li^+(solvent)} + x\,\mathrm{e^-}$$

Reduction:

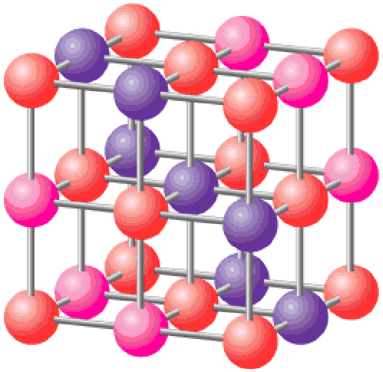
$$\mathrm{C(s)} + x\,\mathrm{Li^+(solvent)} + x\,\mathrm{e^-} \rightarrow \mathrm{Li_{\mathit{x}}C(s))}$$

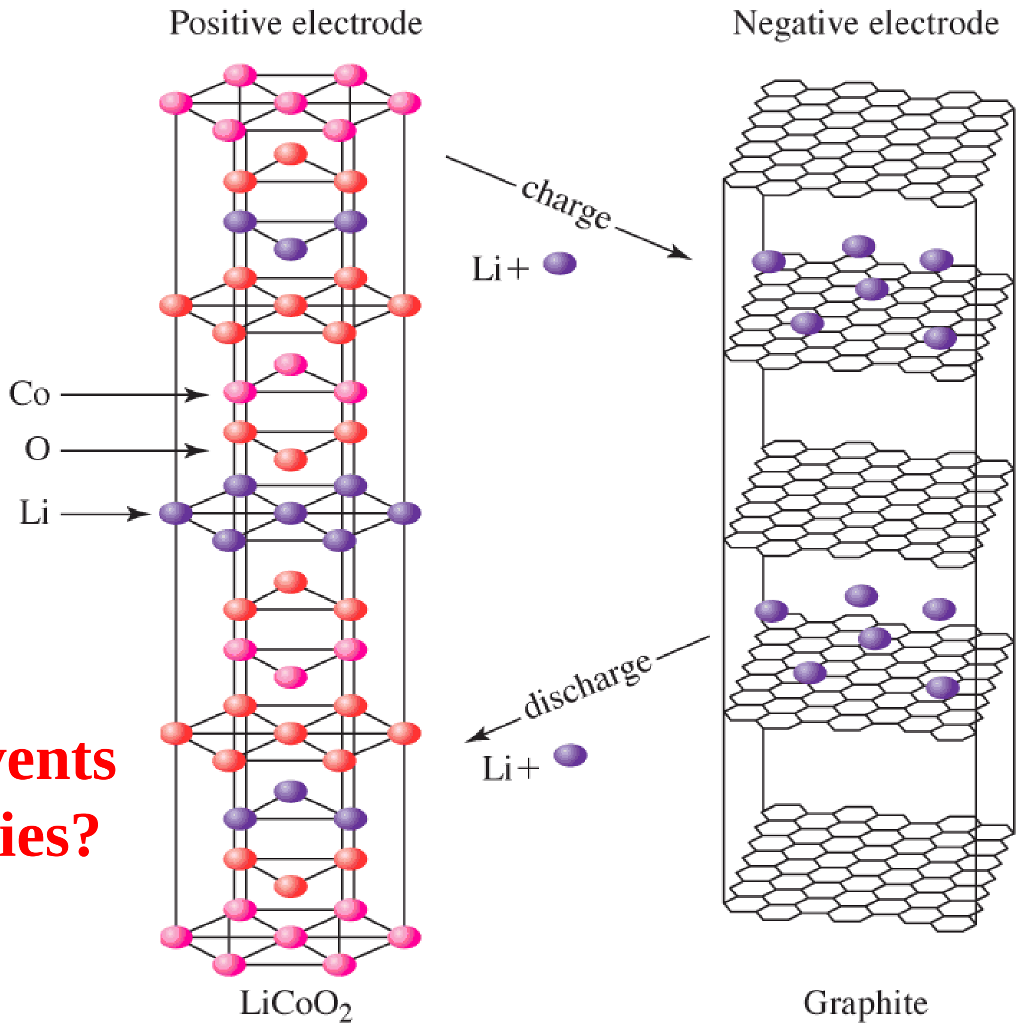
Overall:

$$\mathrm{LiCoO_2(s) + C(s)} \rightarrow \mathrm{Li_{1-\mathit{x}}CoO_2(s)} + \mathrm{Li_{\mathit{x}}C(s)}$$

- high energy density and high-tech
- good for computers, cell phones
- rechargable (secondary cell)
- nonaqueous solvent (such propylene carbonate)
- anode is a non-stoichiometric mixed oxide
- cathode is graphite with inserted Li metal

Lithium-Ion Battery





Why are nonaqueous solvents essential for Li-ion batteries?

Li metal is suitable for high-energy density batteries because it is light and strongly electropositive

$$\mathbf{Li(s) \rightarrow Li^+(aq) + e^-} \qquad \boldsymbol{E^o} = \mathbf{3.04\ V}$$

Aqueous electrolytes can’t be used: in contact with water, Li (also Na and K) spontaneously reduces water:

$$\mathrm{Li(s) \rightarrow Li^+(aq) + e^-} \qquad 3.04\ \mathrm{V}$$

$$\mathrm{e^- + H_2O(l) \rightarrow \tfrac{1}{2}\,H_2(g) + OH^-} \qquad -0.83\ \mathrm{V}$$

$$\mathbf{Li(s) + H_2O(l) \rightarrow Li^+(aq) + \tfrac{1}{2}\,H_2(g) + OH^-(aq)} \qquad \mathbf{2.21\ V}$$

Fuel Cells ("Flow" Batteries)

- Batteries must be replaced (**primary cells**) or recharged (**secondary cells**) when the reactants in the anode or cathode compartments are used up

- In a fuel cell, fresh reactants are pumped into the anode and cathode compartments, and reaction products are pumped out

- Fuel cells can be operated continuously

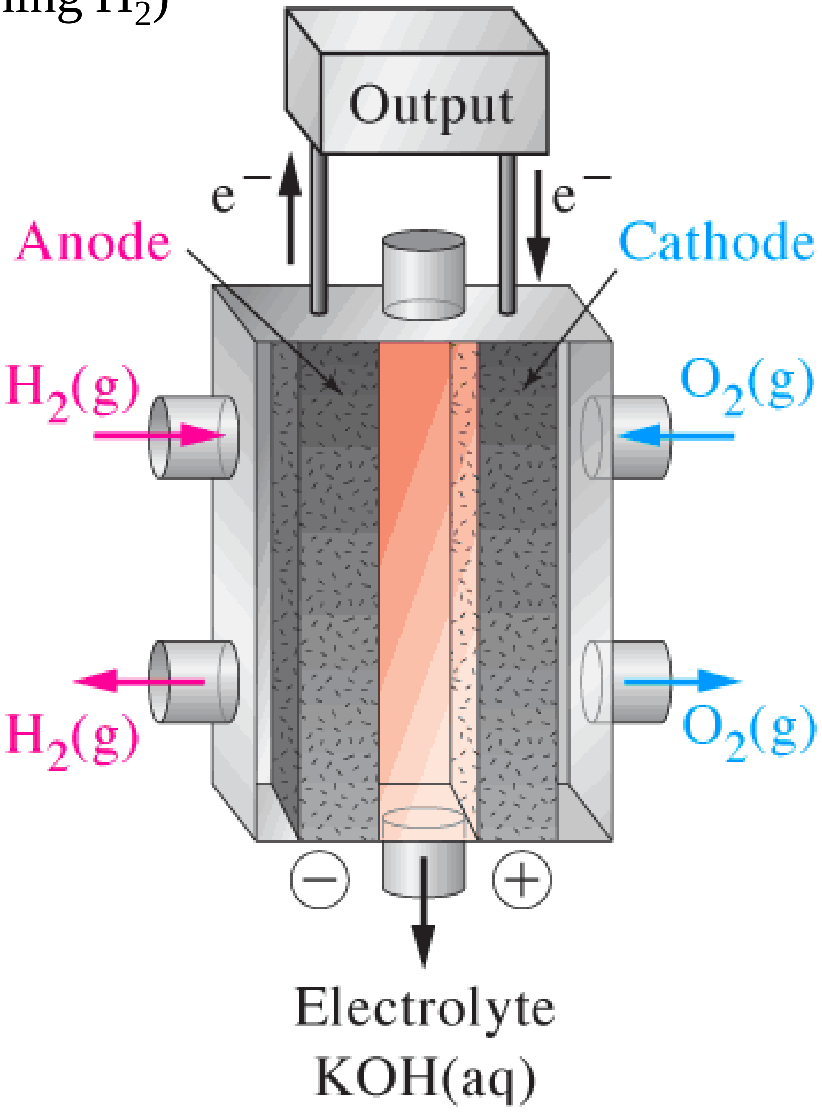
- Chemical energy is converted directly into electrical work

- Fuel-cells can be more efficient than heat engines because their performance is subject to the Carnot limitation :

$$\left| w \right| / q_H = 1 - (T_C / T_H)$$

Hydrogen/Oxygen Fuel Cell (E^o 1.23 V)

(≈ twice as efficient as a heat engine burning H_2)



Anode:

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

Cathode:

$$4e^- + O_2(g) + 2H_2O(l) \rightarrow 4OH^-(aq)$$

Overall:

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

No CO_2 or pollutant emissions!

"Green" source of energy!

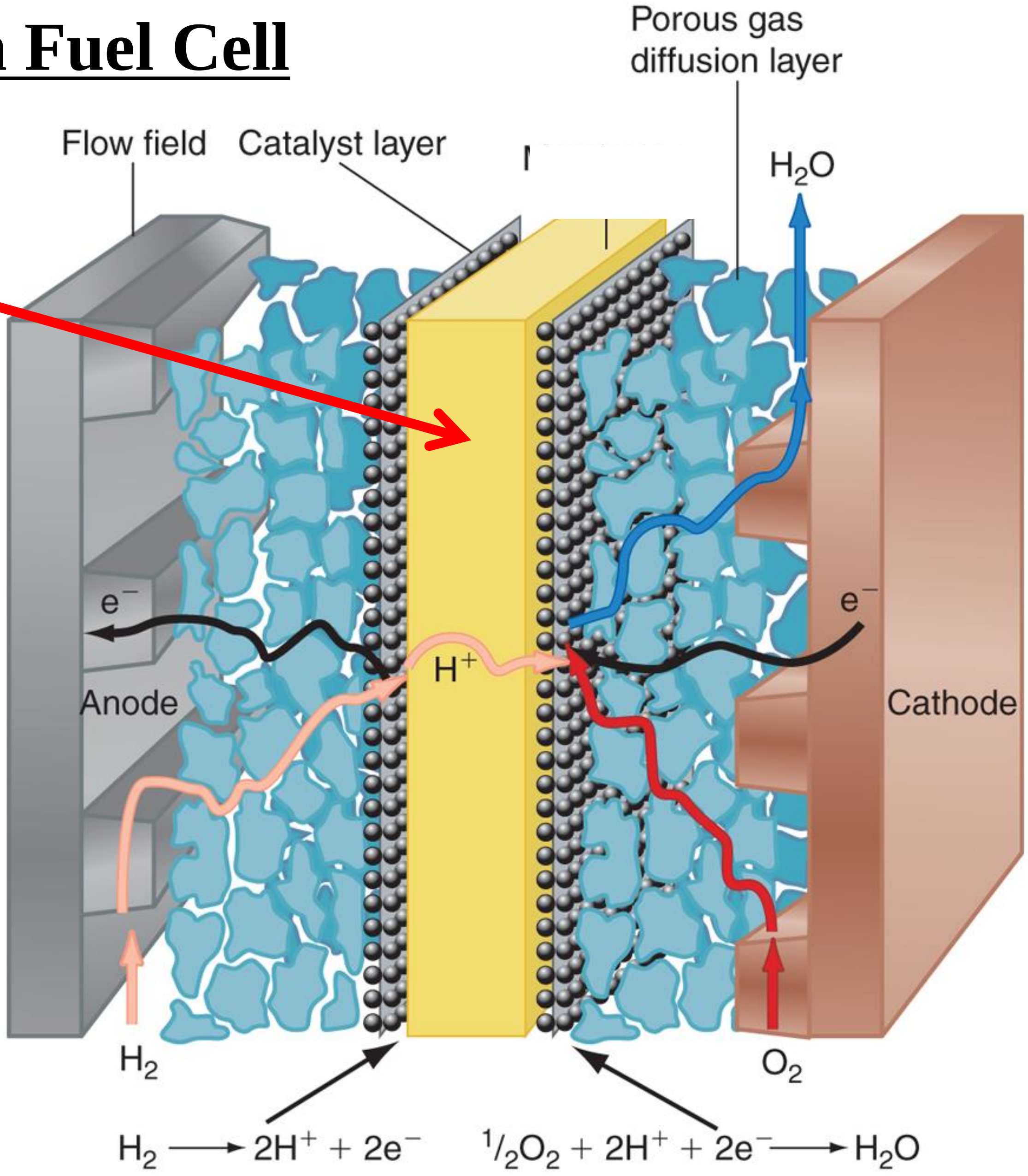
Wow! (Well, *maybe*.)

Expensive.

Hydrogen/Oxygen Fuel Cell

Proton-Exchange Membrane (PEM)

- 10 to 100 μm thick
- solid electrolyte
- conducts H^+ ions (not electrons or anions)



Corrosion: *Unwanted* Spontaneous Electrochemical Reactions

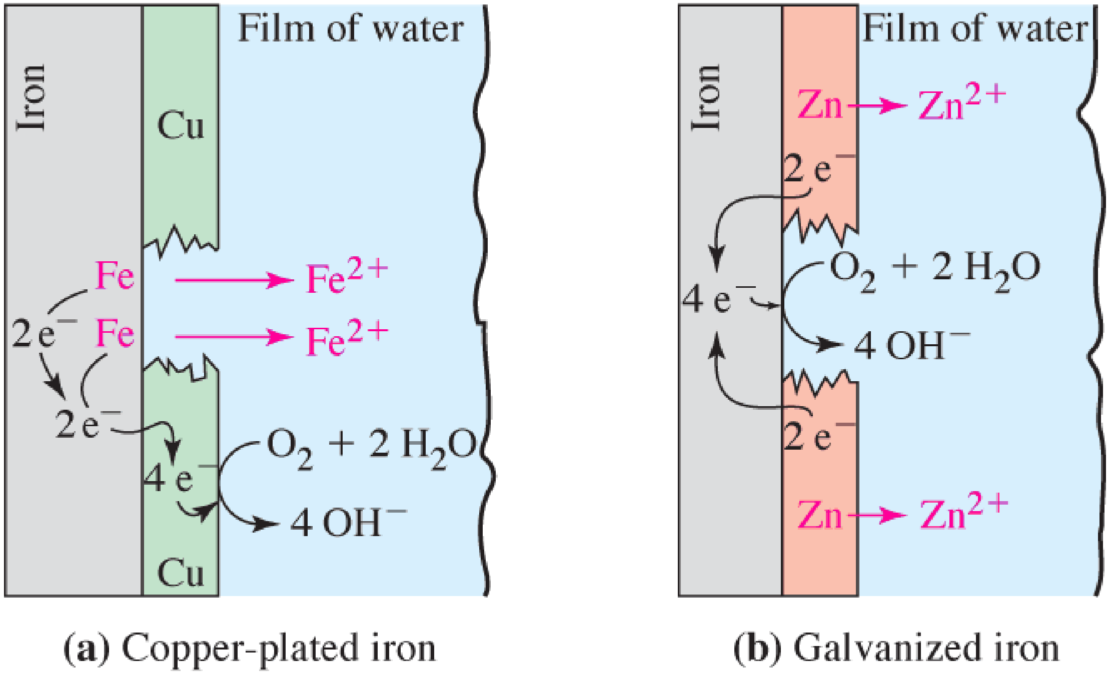
- Corrosion (*e.g.*, “rust”) damages metals in vehicles, machinery, buildings, bridges, pipelines, and other structures

- Corrosion costs trillions of dollars per year

- Corrosion is electrochemical

Why not use metals that don’t corrode (such as stainless steel)?

Protection of Iron Against Corrosion



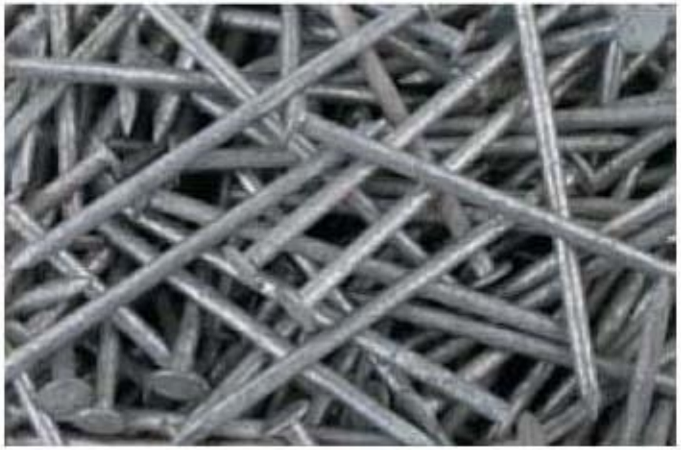
Why is corrosion <u>electrochemical</u>?

Good: Coat iron with copper or another metal less easily oxidized than iron. But watch out! A scratch or pinhole in the coating leads to rapid iron corrosion.

Better: Coat iron with a metal more easily oxidized than iron (such as zinc) that will corrode first, protecting the iron.

“Galvanized” iron and steel:

coated with a protective layer of zinc



But when the zinc is gone, then rust begins!

Sacrificial Magnesium Anodes for the Corrosion Protection of the Steel Hull of a Ship

Seawater serves as the electrolyte.

Electrolysis: Non-spontaneous Reactions *Can Occur !*

Batteries, fuel cells, corrosion (“passive” electrochemistry) **:**

- spontaneous chemical reactions
- generate voltages and electrical currents

Electrolysis cells (“active” electrochemistry)**:**

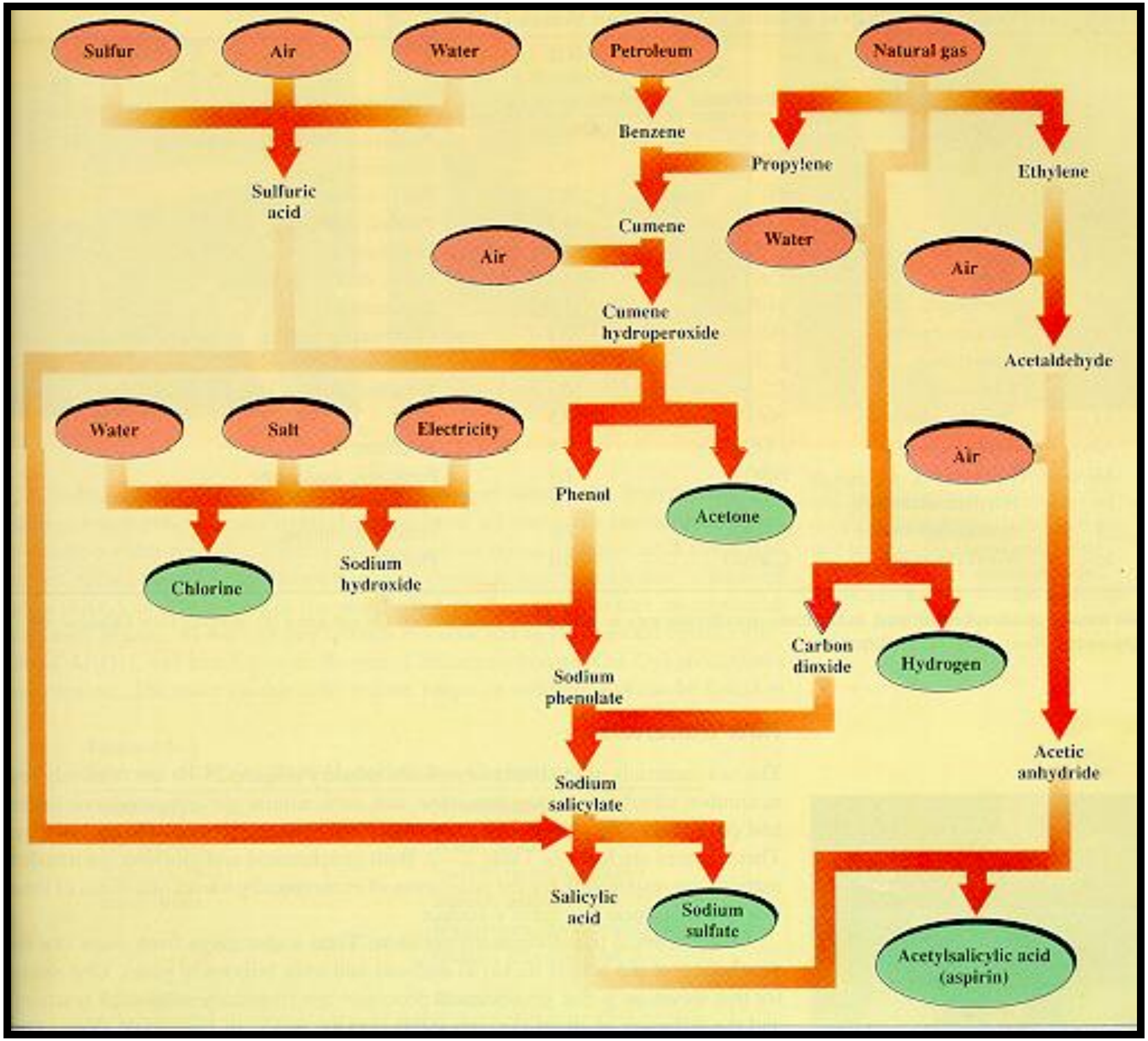
- apply voltages to drive non-spontaneous reactions
- make chemicals never found in nature

Chlor-Alkali Production

- Electrolysis of aqueous NaCl solutions
- Cl_2, NaOH, and H_2 are produced
- Largest electrochemical industry
- **70 % of all chemicals produced use Cl_2 or NaOH in one or more of the synthetic steps**

Why are there no natural deposits of Cl_2, NaOH, and H_2?

Flow Sheet for Industrial Aspirin Production from:



- natural gas
- petroleum
- air
- **water**
- **salt**
- sulfur

Diaphragm Chlor-Alkali Cells (“low-tech”, but effective)

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

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

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

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

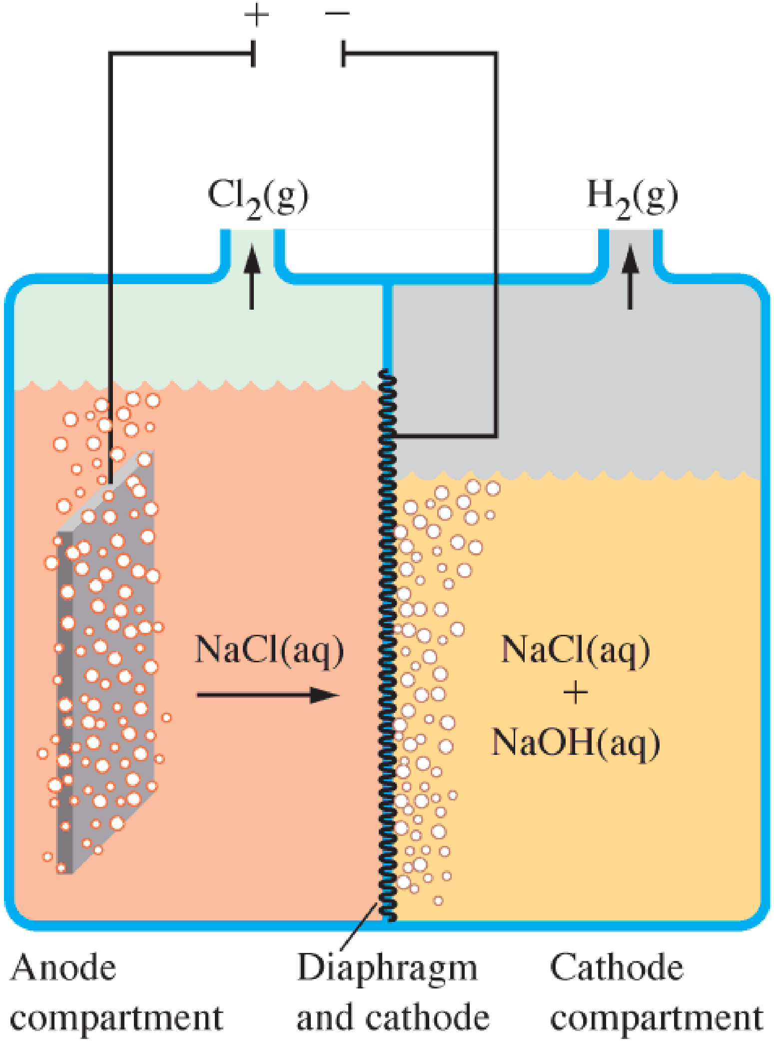
Overall ($E^o = -1.36 - 0.83 = -2.19$ V):

$2Cl^-(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2OH^-(aq)$

Why is *E*º for the cell reaction negative?

Typical applied cell voltages are ≈ −3.0 V, significantly larger than *E* º. *Why*?

Porous asbestos diaphragms are being replaced with Na^+-ion- permeable membranes in modern chlor-alkali plants.



Aluminum Production

- aluminum metal cannot be produced by reducing aqueous Al^{3+} ions (*Why*? Water is reduced before Al^{3+}.)
- instead, Al_2O_3 (alumina) is electrolyzed in a **molten salt electrolyte** (cryolite, Na_3AlF_6)
- second-largest electrochemical industry (after chlor-alkali)
- before the development of electrochemical processes, aluminum metal was more valuable than platinum or gold!

Cryolite Electrolysis Cell for Aluminum Production

Carbon Anode (consumable):

$O^{2-}(melt) + C(s) \rightarrow CO_2(g) + 2e^-$

Steel Cathode:

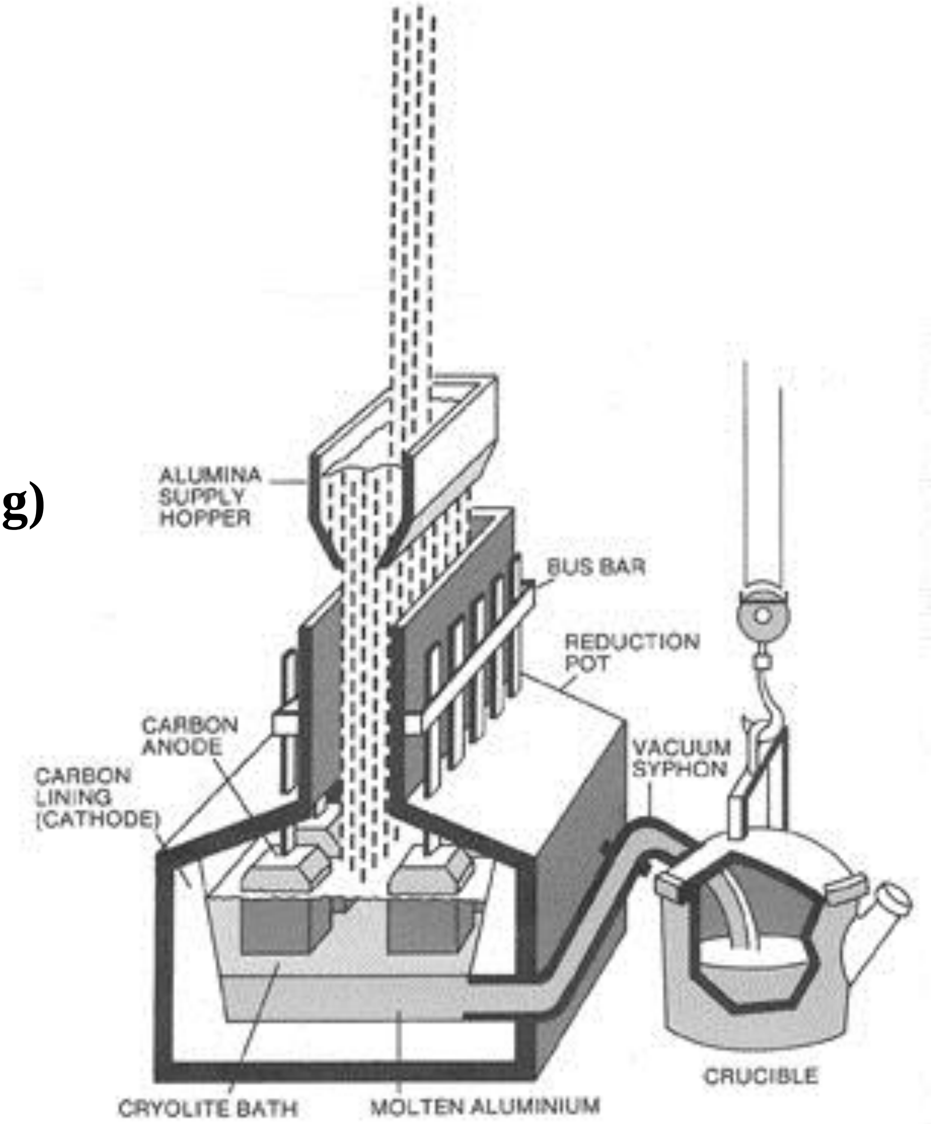
$3e^- + Al^{3+}(melt) \rightarrow Al(l)$

Overall:

$2Al_2O_3(melt) + 3C(s) \rightarrow 4Al(l) + 3CO_2(g)$

Why do the consumable carbon anodes reduce the voltage that must be applied to the electrolysis cell?

The alumina/cryolite molten electrolyte is near the eutectic composition. Why does this reduce operating costs?



(≈ 1000 ºC)

Copper Electrorefining

Impure copper anode:

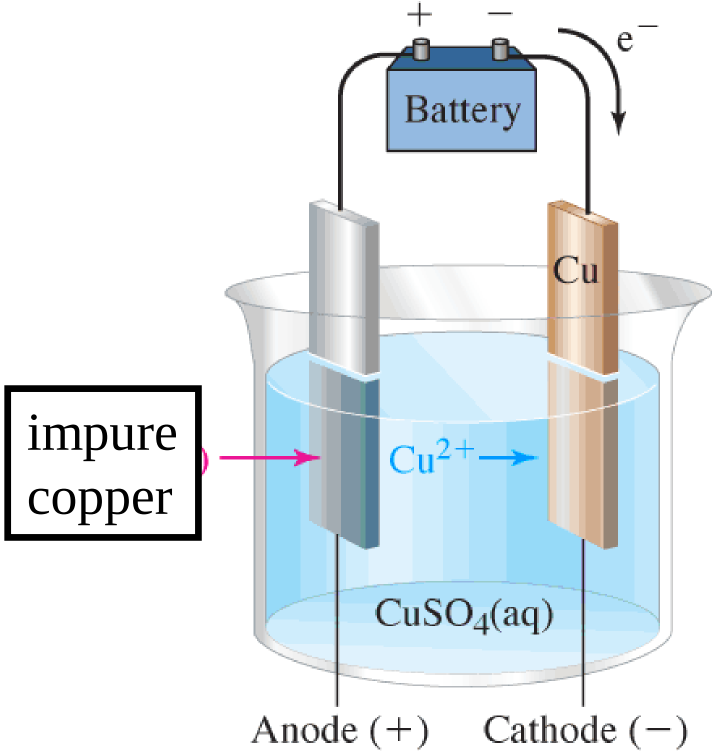
$\mathrm{Cu(s, impure)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2e^{-}$

Pure copper cathode :

$2e^{-} + \mathrm{Cu^{2+}(aq)} \rightarrow \mathrm{Cu(s, 99.99\ \%\ pure)}$

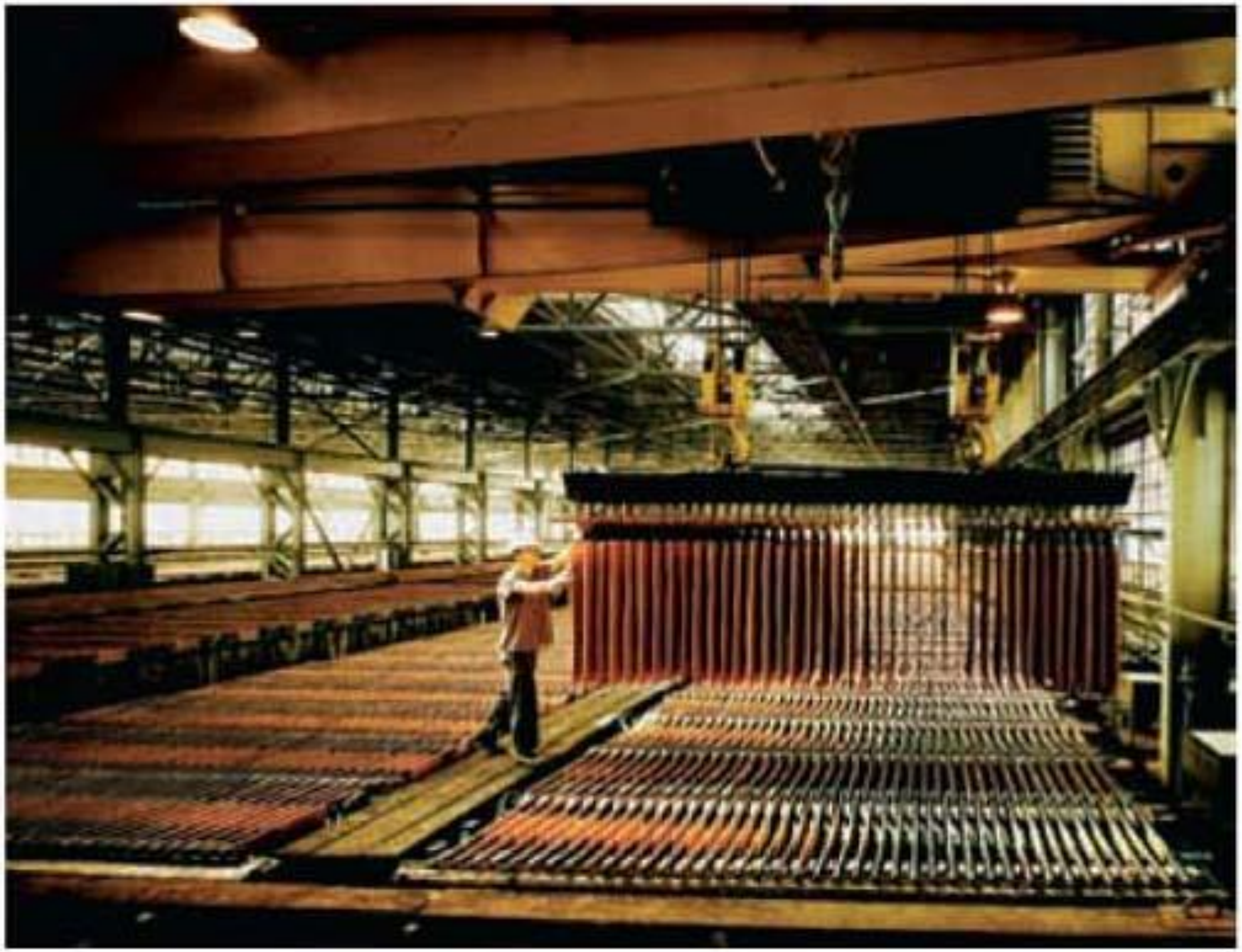
Overall:

$\mathrm{Cu(s, impure)} \rightarrow \mathrm{Cu(s, pure)}$


impure copper

Zn, Pb, Fe, Ag, and other impurities remain in solution or precipitate as sludge.

Cell House for Copper Electrorefining



High-purity copper is mechanically scraped off the cathodes.

Electroplating

Cells similar to those used for copper refining can also be used to coat metal objects with a layer of electrolytically-deposited pure copper.

Nickel, chromium, tin, silver, zinc (“galvanized” steel), and many other metals can be **electroplated**.

Electroplating can provide tough, durable, corrosion-resistant, or decorative surfaces.

A rack of metal parts being lifted from the electrolyte solution after electroplating.

Electrolysis of Water: H_2 and O_2 Production

Anode ($E^{o} = -1.23$ V):

$2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$

Cathode ($E^{o} = -0.83$):

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

Overall ($E^{o} = -1.23 - 0.83 = -2.06$ V):

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

Not **an important industrial process!**

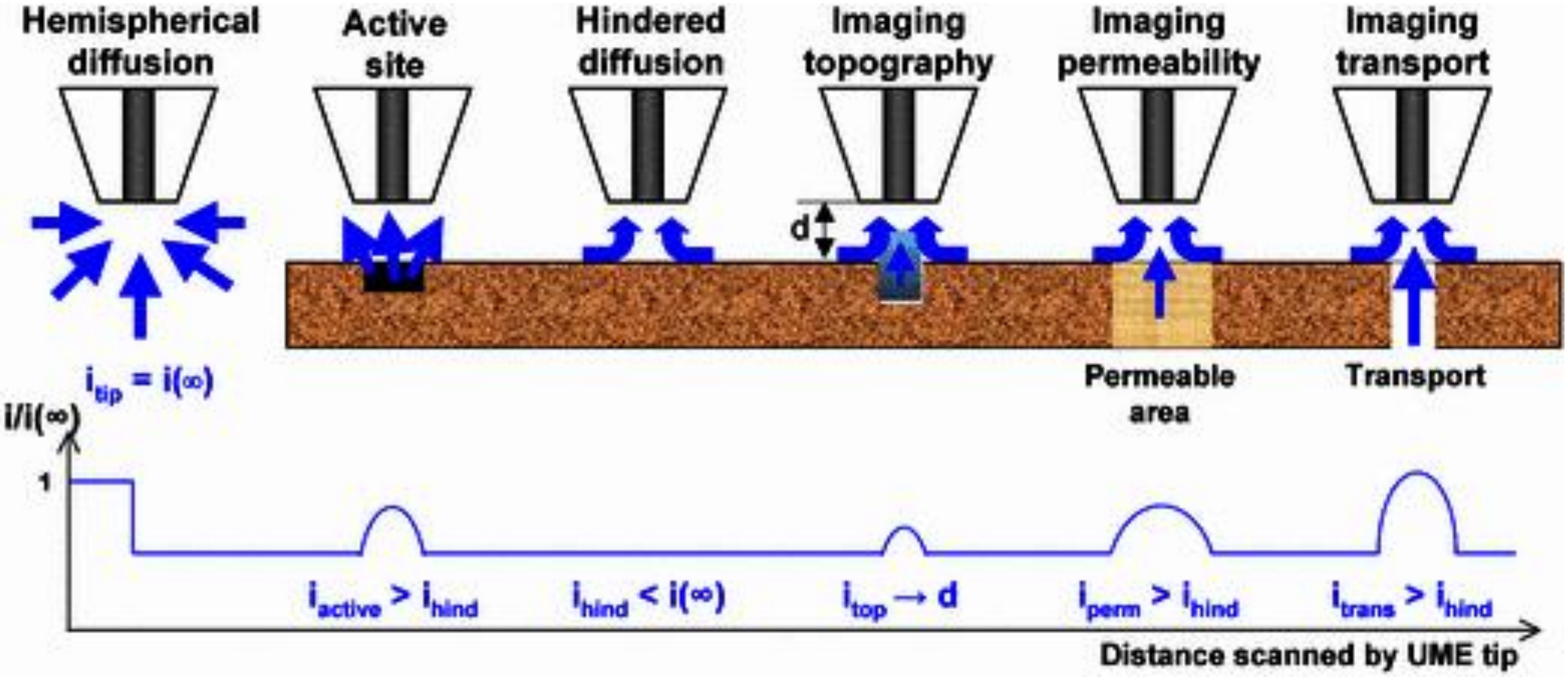
>99% of industrial hydrogen is produced by the much cheaper steam-reforming of natural gas: $CH_4(g) + H_2O(g) \rightarrow 3H_2 + CO(g)$.

Oxygen is produced industrially by the fractional distillation of liquid air.

Which is the anode?

Sections 11.14 Electrochemical Microscopes

- scan "ultramicroscopic" electrodes (UME's) over surfaces
- measure electrochemical current at different positions



Sections 11.15 Electrochemical Machining

- shape metal parts electrochemically
- independent of material hardness
- suitable for intricate shapes, curved surfaces, square holes