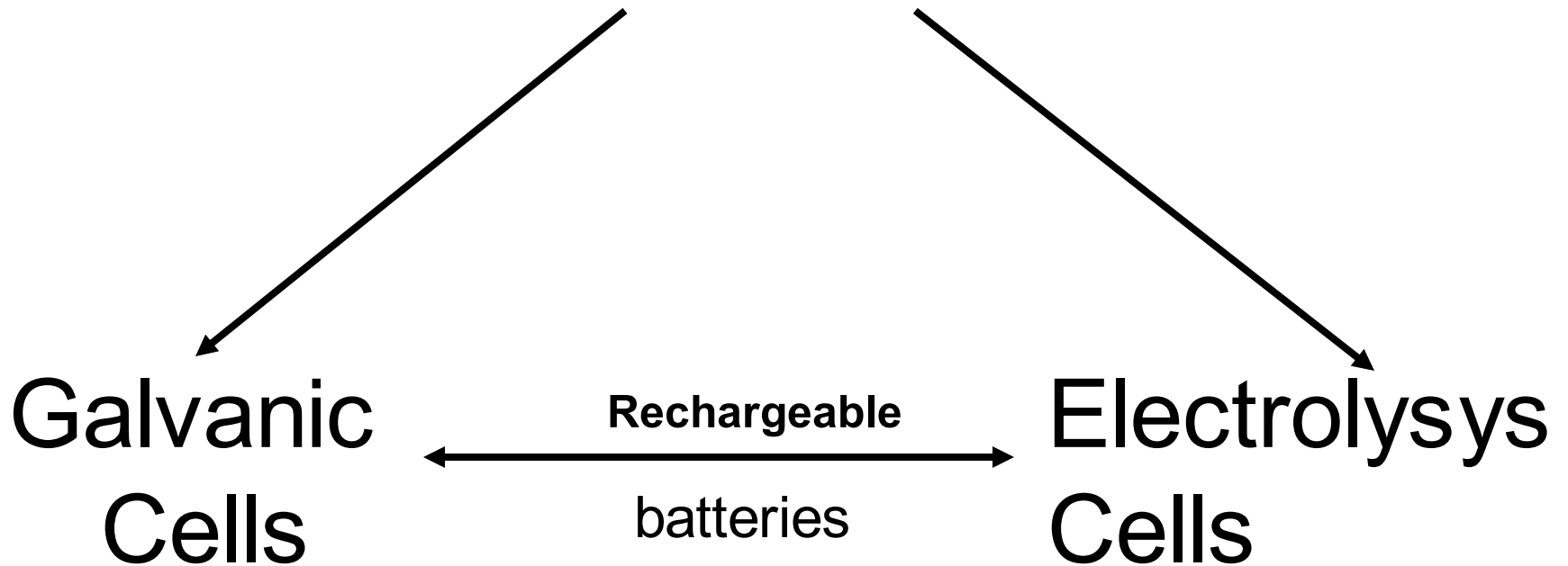


Electrochemistry

Two broad areas



Electrochemistry

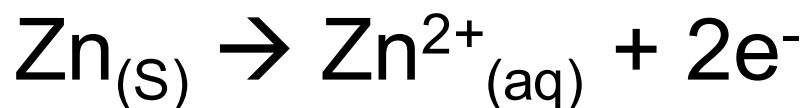
Batteries, or galvanic cells, use an electron transfer (oxidation/reduction) reaction to produce a flow of electrons.

Review the handouts
on predicting products and balancing redox reactions.

Electrochemistry

An electron transfer reaction:

$\text{Cu}^{2+}_{(\text{aq})} + \text{Zn}_{(\text{s})} \rightarrow ?$ The half rxns. are:

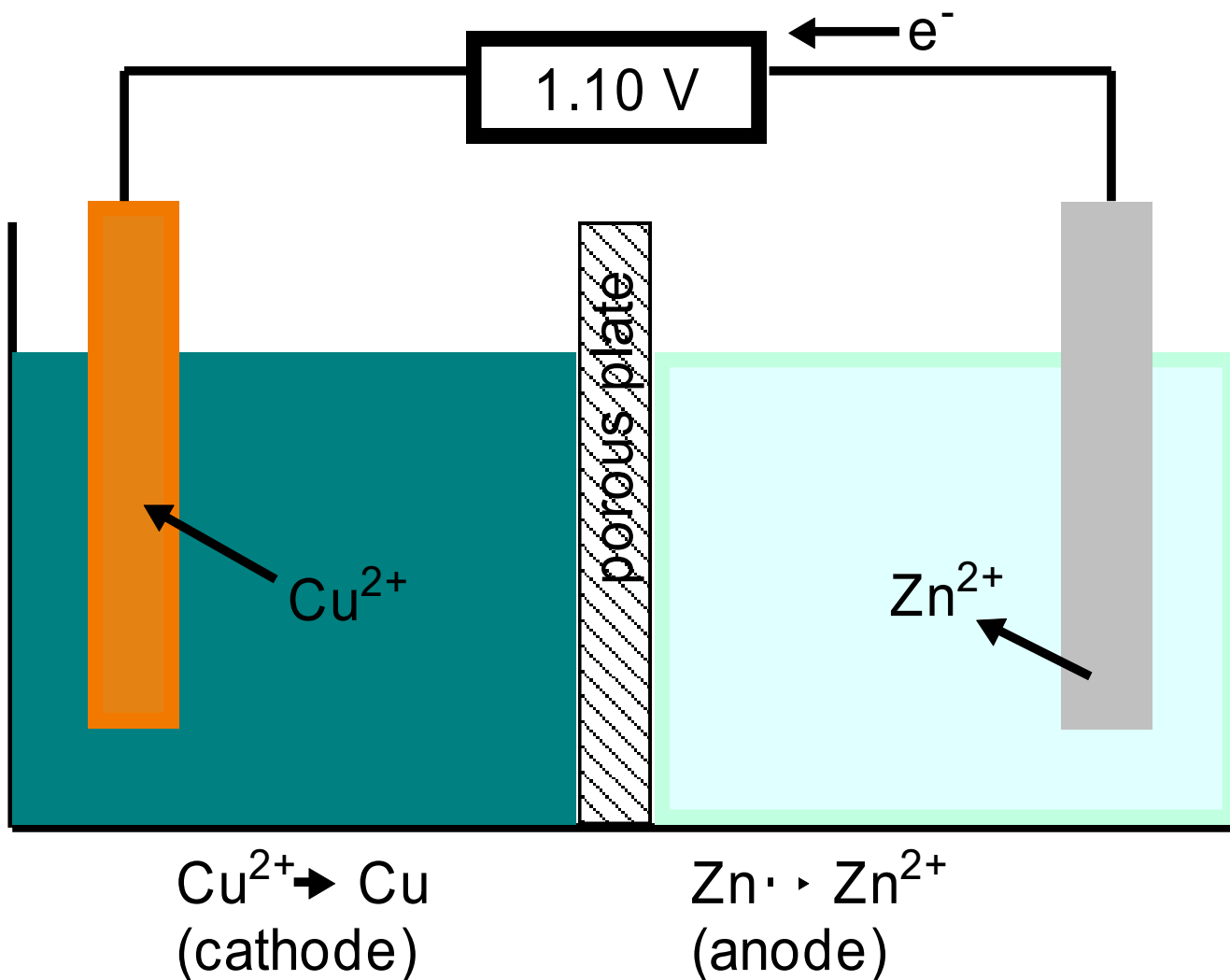


In the usual way zinc dissolves and copper is precipitated from solution.

BUT It is possible to separate the two half reactions, linking them by a wire and a salt bridge or porous plate.

Electrochemistry

Daniel Cell



Electrochemistry

The Hydrogen electrode



$$[\text{H}^+] = 1 \text{ M},$$

$$P = 1 \text{ atm},$$

$$T = 25^\circ\text{C}$$

Electrochemistry

Standard Reduction Potentials

Standard Reduction Potentials are found vs. the standard hydrogen electrode.

E.g. $\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2$ (all at Std. State)

$$V^\circ_{\text{cell}} = 0.76 \text{ Volts}$$

$$V^\circ_{\text{cell}} = V_{\text{H}} + (-V_{\text{Zn}}) \text{ therefore}$$

$$V_{\text{Zn}} = -0.76 \text{ volts and, from Daniel Cell}$$

$$V_{\text{Cu}} = 0.34 \text{ volts}$$

Electrochemistry

Standard Reduction Potentials



or



$$V_{\text{Fe}^{3+}/\text{Fe}^{2+}} = V^{\circ} - V_{\text{Cu}} = 0.43 - (-0.34) = 0.77 \text{ volts}$$

We may use this method to calculate any reduction potential.

Electrochemistry

- Half cell voltages are usually tabulated as reduction potentials.
- $E > 0$ (the cell voltage is positive) for any spontaneous process.
- 1 volt = 1 joule/coulomb or $E = -w/\text{charge}$
- therefore $w = -\text{charge} \times \text{volts}$ & $\text{charge} = nF$

This is w_{max} since some energy is lost to frictional heating. I.e. entropy increases.

Electrochemistry

- $w_{\max} = \Delta G = -nfE_{\max}$ where $E_{\max}$ is the maximum voltage of the cell

- $\Delta G^\circ = -nfE^\circ$

for the Daniel cell

$$E^\circ = 1.10 \text{ volts}$$

$n = 2/\text{mole of product \&}$

$$\Delta G^\circ = -2\text{mol} \cdot 96,485 \text{ coul/mol} \cdot 1.10 \text{ J/coul}$$

$= -212 \text{ kJ}$ & the process is spontaneous
as written

Electrochemistry

Remember,

$\Delta G = \Delta G^\circ + RT \ln Q$, therefore,

$-nfE = -nfE^\circ + RT \ln Q$, or

$nfE = nfE^\circ - RT \ln Q$, or

$$\mathbf{E = E^\circ - (RT/nf) \ln Q = E^\circ - (0.059/n) \log Q}$$

This is the **Nernst Equation**

At equilibrium, we have

$$\mathbf{E^\circ = (0.059/n) \log K_{eq}}$$

Electrochemistry

One consequence of this is it is possible to build a galvanic cell where the only difference between the cathode and anode is the concentration of reactive species.

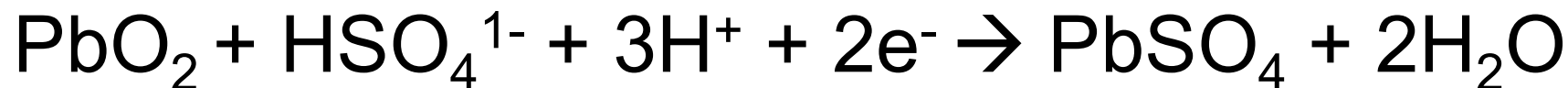
E.g. $M^{n+} \rightarrow M^{n+}$

$\frac{1.0M}{\quad} \quad \frac{0.1M}{\quad}$

$$E = 0 - \frac{0.059}{n} \log(0.1/1.0) = \frac{0.059}{n} \text{ volt}$$

Real-World Batteries

Lead storage:

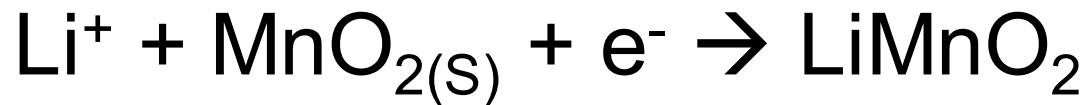


A set of lead grids alternately filled with spongy lead and spongy lead(II) oxide

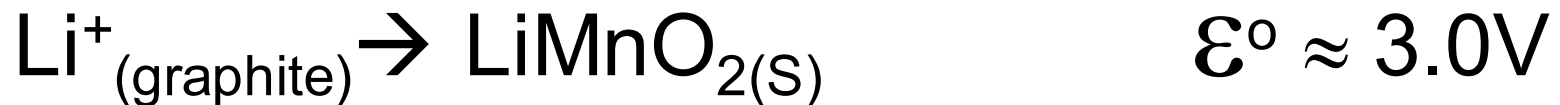
$V_{\text{cell}} \approx 2.2$ volts, reaction is reversible

Electrochemistry

the lithium and lithium ion battery



or, “lithium ion”



Electrochemistry

Rusting

Iron is not homogeneous. It is a mixture of iron, a little carbon and often other transition metals. Also, there are stressed regions. Some of these regions are anodic (e^- sources) while others are cathodic.

Iron is oxidized in the anodic region, if water is present. $\text{Fe}_{(s)} \rightarrow \text{Fe}^{2+} + 2e^-$

The iron(II) migrates through the water to a cathodic region

Electrochemistry Rusting

Iron is oxidized in the anodic region, if water is present. $\text{Fe}_{(\text{s})} \rightarrow \text{Fe}^{2+} + 2\text{e}^{-}$

The iron(II) migrates through the water to a cathodic region, where:

$\text{O}_2 + \text{H}_2\text{O} + 4\text{e}^{-} \rightarrow 4\text{OH}^{-}$ has taken place

There is a further reaction with oxygen:

$2\text{Fe}^{2+} + \text{O}_2 + 2\text{OH}^{-} \rightarrow \text{Fe}_2\text{O}_{3(\text{s})} + \text{H}_2\text{O}$

So “rust” build up and a hole appears

Electrolysis

The use of an electric current to create a chemical change. I.e. charging a storage battery.

Note: You must drive a chemical reaction. The required voltage to cause a chemical change is always greater than the voltage one would see in the reverse reaction.

Electrolysis

To solve electrolysis problems, find:

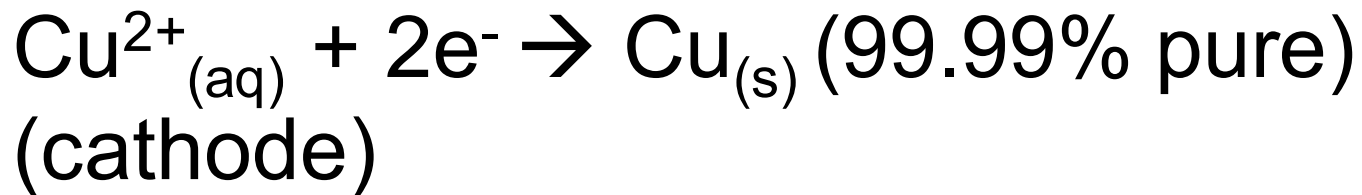
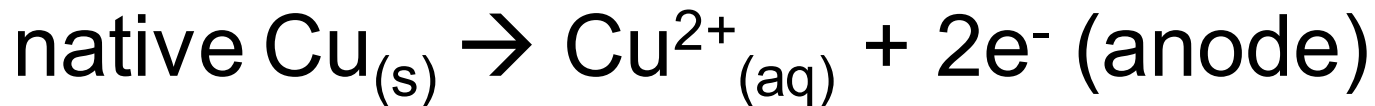
1. Current and time →
2. Charge in coulombs →
3. Faradays (moles of e^- s) →
4. Moles of product(s) →
5. Mass of product(s)

for example:

Electrolysis

How many pounds of pure copper could be produced by a current of 100 amps flowing for 1 week?

Pure copper is produced as follows:



Anode residue contains Au, Ag Pt, etc.

Electrolysis of salt water

- $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ $E^\circ = -1.36$ volt
- $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ $E^\circ = -1.23$ volt
- $2\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ $E^\circ = 0.00$ volt

∴ Would seem the electrolysis products are:
 H_2 & O_2 . But they are H_2 & Cl_2 because the overvoltage for water to oxygen is very high.
So, **the products are H_2 , Cl_2 & NaOH .**

In fact, this electrolysis is a major source of both chlorine and sodium hydroxide.

Electrolysis of aluminum oxide

The Hall-Heroult Process

A mixture of Al_2O_3 and cryolite (NaAlF_6) is melted and electrolyzed using a graphite-lined tank as the cathode and graphite rods as the anodes. The reaction produces CO_2 at the anodes and liquid aluminium at the cathode. Rxn: $2 \text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2$

Cost of 1 # of Al: 1855, \$100,000
 1890, \$2