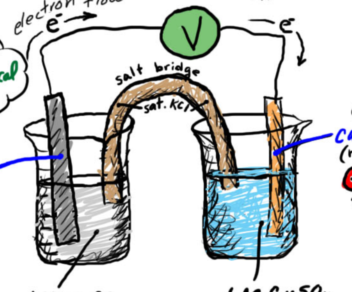
ELECTROCHEMISTRY

VOLTAIC CELL

spontaneous chem rxn provides electrical ENERGY!

← I — electric current flow (opposite of e^- flow)

electron flow e^- → V → e^-



Zn anode (oxid) − sign

Cu cathode (red.) + sign

1 M $ZnSO_4$ | 1 M $CuSO_4$

note that this is the "flipped" version of this rxn off the table

½ rxn $Zn \rightarrow Zn^{2+} + 2e^-$ | ½ rxn $Cu^{2+} + 2e^- \rightarrow Cu$

$\mathcal{E}^\circ_{ox} = +.76\,V$ | $+.34\,V = \mathcal{E}^\circ_{red}$

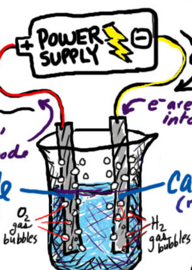
net ionic rxn

$$Zn + Cu^{2+} \xrightarrow{2e^-} Zn^{2+} + Cu$$

$$\mathcal{E}^\circ = +1.10\ V$$

ELECTROLYTIC CELL

electrical energy is used to FORCE a non-spontaneous rxn to occur!



e^- are "PULLED" out of anode | e^- are "PUSHED" into cathode

anode (oxid) + | cathode (reduct.) −

½ rxn $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

½ rxn $(2H_2O + 2e^- \rightarrow H_2 + 2OH^-) \times 2$ to get electrons to balance

net rxn: $6H_2O \rightarrow 2H_2 + O_2 + 4H^+ + 4OH^-$ make $4H_2O$'s which will cancel 4 on the other side

net rxn leads to $\boxed{2H_2O \rightarrow 2H_2 + O_2}$

NERNST

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF}\ln Q$$

$$\mathcal{E} = \mathcal{E}^\circ - \frac{.0257}{n}\ln Q$$

$$\mathcal{E} = \mathcal{E}^\circ - \frac{.05916}{n}\log Q$$

for calculating potentials @ NON-std conditions!

Reduction: the GAIN of e^- (ox# decreases)

Oxidation: the LOSS of e^- (ox# increases)

$$\mathcal{E}^\circ_{cell} = \mathcal{E}^\circ_{red} + \mathcal{E}^\circ_{ox}$$

off the table | this is a "flipped" value! | opposite sign as that on table

S.H.E. standard hydrogen electrode

$2H^+ + 2e^- \rightleftharpoons H_{2\,(g)}$

assigned 0.000000... volts* by IUPAC agreement

* at all temperatures

counting coulombs...

you need the Faraday constant

$$F = 96485\ C/1\,mol\ e^-$$

this is our unit factor to get from "electricity world" which is full of volts, amps, & time and into "chemistry world" which is moles of stuff

$$\frac{I \cdot t}{n\ F} = \text{mol of stuff}$$

I: current in amps or C/s; t: time in seconds; n: number of e^- transferred; F: 96485 C/mol e^-

this formula works for any ½ rxn & the "mol of stuff" is whatever you are after in the ½ rxn — great for electrodepositions!

triforce of chemistry

$$\Delta G^\circ = -RT\ln K$$

wow! cool! neato!

$$\Delta G^\circ = -nF\mathcal{E}^\circ$$

$$\mathcal{E}^\circ = \frac{RT}{nF}\ln K$$

Shorthand cell notation

phase boundaries

anode | anodic solution || cathodic solution | cathode

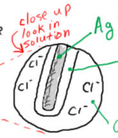
left side is always anode oxidation! | salt bridge | right side is always cathode reduction!

★ If there are SOLIDS (salts) as part of the ½ rxn then the solid must be in contact (coating) with the electrode. Gases must be bubbled over the electrode

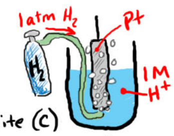
$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-$

is shown as cathode like this $||\ Cl^-\ |\ AgCl\ |\ Ag$

probably a 1 M NaCl solution | coating ON the silver wire



IF the ½ rxn has no conductor (metal) in it, use an INERT electrode like platinum (Pt), gold (Au), or graphite (C)



→ for S.H.E. you use a Pt electrode in 1 M H^+ with 1 atm $H_{2\,(g)}$ bubbling over the surface

shorthand → $Pt\ |\ H_2\ |\ H^+\ ||$ ← shown as anode (on the left)

BATTERIES

★ PRIMARY: Rxn is not reversible NOT rechargeable → ALKALINES, Lithium, "Heavy Duty"

★ Secondary: Rxn is reversible RECHARGEABLE! → NiCads (mostly banned), NiMH, Li-ion (cell phones, digital cameras), Pb-storage (aka: Pb-acid or car battery)

★ Fuel Cells: you REFILL with reactants (not recharged) → H_2/O_2, Zn-air

CAR BATTERY (Pb-acid)

the lead is in 3 different oxidation states in this battery

$Pb_{(s)}$ (0), $PbSO_{4\,(s)}$ (+2), $PbO_{2\,(s)}$ (+4) — NOTE these are ALL solids!

on discharge... (its a voltaic cell)

anode: $Pb_{(s)} + HSO_4^- \rightarrow PbSO_{4\,(s)} + 2e^- + H^+$

cathode: $PbO_{2\,(s)} + 3H^+ + HSO_4^- + 2e^- \rightarrow PbSO_{4\,(s)} + 2H_2O$

overall: $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

this is the charged state of the battery | this is sulfuric acid so you could write it as $2H^+ + 2HSO_4^-$ showing it 100% ionized | this is the discharged state → aka: a dead battery

Cool! the sulfuric acid is consumed during discharge & more water is made.

What about Recharge? → just flip all the rxns & change the names of the electrodes → its now an electrolytic cell.

SIZE MATTERS

cells AAA AA C D

All 4 are 1.5V

so what does size get you? More current! which means more POWER!

But how? more material & most important, bigger surface area for electrodes = more e^- transferred