Ch. 19 Electrochemistry and it's Applications

e^- flow = electricity

electrochem = study of e^- transfer

Product-favored

① Spontaneous redox runs batteries

② Voltmeters quantify electrochem

- measure reactivity of redox

③ Reactant favored redox can be pushed to product side by external electricity

"Electrolysis, electroplating" - source of many pure metals not found in nature

[illegible]

$Cr^{3+} + 3e^- \rightarrow Cr$ (chrome-plating)

- [illegible]

$2Cl^- \rightarrow Cl_2$ (for disinfecting water

④ "Corrosion", "rusting" are redox processes to <u>prevent</u>

19-2

19.1 Redox Reactions (Review: 5.3)

ex $2Al + 3ZnBr_2 \longrightarrow 3Zn + 2AlBr_3$

<u>Recognizing</u>:

① Presence of an <u>element</u>
(in reactant or product side)

② Change in "oxidation number" (Review 5.4)
- counts charge in molecular as well as ionic compounds
- in a polar covalent bond, more electronegative atom is given negative charge (credited with bonding e's) + vice versa

$\overset{\delta+}{H}-\overset{\delta-}{Cl}$ $\qquad$ $\overset{\delta-}{O}=\overset{\delta+}{C}=\overset{\delta-}{O}$

$H^{\oplus}\ Cl^{\ominus}$ $\qquad$ $O^{2-}\ C^{4+}\ O^{2-}$

$\boxed{\text{Handout}}$ $\qquad$ $\boxed{\text{Practice Problems}}$

<u>Notes, Terms</u>

① Oxidation: loss of e's
- Ox # increases (more positive or less neg)

$Al^0 \rightarrow Al^{3+}$

ex $-3 \rightarrow -1$, $+2 \rightarrow +4$

Assigning Oxidation Numbers

This is a more complete set of rules than your text book. It always works.

Use these rules in order.
The sum of all oxidation numbers of all elements = charge on substance

		Oxidation Number:	Examples:
1.	**Atoms in their elemental state**	=0	Fe, H_2, O_2
2.	**Monatomic ions**	=charge	F^{1-}, Na^{1+}, Fe^{3+}

IN COMPOUNDS

3.	**Group 1A**	=+1	NaCl, KNO_3
4.	**Group 2A**	=+2	MgO
5.	**Fluorine**	=-1	HF, ClF
6.	**Hydrogen**	=+1	H_2O
7.	**Oxygen**	=-2	SO_2, $HClO_4$
8.	**Group 7A**	=-1	HCl
9.	**Group 6A**	=-2	PbS_2

Try these:

SO_2, $HClO_4$, SO_3, PCl_5, NO_2, SO_4^{2-}, NO_3^{1-}, NO_2^{1-}, ClF_3, F_2

Jasperse-Chem 160 Ch. 19-Problems

Find Ox #'s for

① H_2CO C:

② PCl_3 P:

③ HSO_4^- S:

④ $KMnO_4$ Mn:

⑤ $Mg_3(PO_4)_2$ P:

Identify oxidizing and reducing agents

① $2Na + 2HCl \longrightarrow 1H_2 + 2NaCl$

② $2KMnO_4 + 6NaCl \longrightarrow 2MnO_2 + 3Cl_2$ (some H_2O, KOH, NaCl also involved)

Jasperse—Chem 160 Ch. 19—Problems

$\boxed{\text{Answers}}$

Find Ox #'s for

① H_2CO C: $2+C-2=0$ $\boxed{C=0}$

② PCl_3 P: $P-3=0$ $\boxed{P=+3}$

③ HSO_4^- S: $1+S-8=-1$ $\boxed{S=+6}$

④ $KMnO_4$ Mn: $1+Mn-8=0$ $\boxed{Mn=+7}$

⑤ $Mg_3(PO_4)_2$ P: $\boxed{P=+5}$

PO_4^{3-}

Identify oxidizing and reducing agents

$2\times1e=2$ spectator

① $2Na + 2HCl \longrightarrow 1H_2 + 2NaCl$ $\boxed{2e^- \text{ transfer}}$

oxidized reducing agent | reduced oxidizing agent | $2\times1e^-=2e$

$2\times3e^-$

② $2K\overset{+7}{Mn}O_4 + 6Na\overset{-1}{Cl} \longrightarrow 2\overset{+4}{Mn}O_2 + 3\overset{0}{Cl_2}$ (Some H_2O, KOH, NaCl also involved)

reduced oxidizing agent | oxidized reducing agent | $6\times1e^-$

$\boxed{6e^- \text{ transfer}}$

② Reduction: gain of e's
— Ox # "reduced"
$Zn^{2+} \rightarrow Zn^0$
$0 \rightarrow -1$ $-1 \rightarrow -2$, $+3 \rightarrow +2$

"Leo the Lion says GER!"
losing e's oxidation — gaining reduction

③ "Oxidizing Agent" or "Oxidant"
— causes something else to be oxidized
— itself reduced

"Reducing Agent"
— causes other to get reduced
— itself oxidized

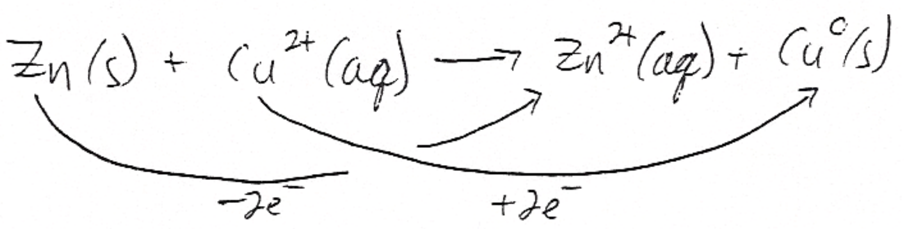
$Al \rightarrow Al^{3+}$ reducing agent
$Zn^{2+} \rightarrow Zn$ oxidizing agent

Practice, 19-3

④ "Redox" reduction – oxidation

⑤ e's must balance

19.2 Half Reactions, Redox, and balancing



$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu^{0}(s)$$

- both ox and red must occur
- e's must balance

Half Reactions

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

Red: $2e^- + Cu^{2+} \rightarrow Cu^0$

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

Suppose

Ox: $2Na \rightarrow 2Na^+ + 2e^-$ ⇐ need coef. of 2

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

Net $2Na + Zn^{2+} \rightarrow Zn + 2Na^+$

Balancing Redox

① Set coefficients so $\boxed{\#e\text{'s released} = \#e\text{'s accepted}}$
- focus on atoms where ox # changes

② balance redox spectators

Make sure:

a) charges balance
b) atoms balance

Note: test problems I will give you all species involved

19-6

<u>Balance</u> (Test Level)

① $H^+ + I^- + NO_3^- \rightarrow I_2 + NO + H_2O$

② $H_2O + MnO_4^- + Br^- \rightarrow MnO_2 + BrO_3^- + OH^-$

<u>OWL:</u>

① Acid conditions: balance, adding H_2O's and H^+'s as needed

$ClO_3^- + SO_2 \rightarrow Cl_2 + SO_4^{2-}$

② Base: end with H_2O's, OH^- as needed (long!!)

$MnO_4^- + SO_2 \rightarrow MnO_2 + SO_4^{2-}$

Balance (Test Level)

$3 \times 2e^- = 6e^-$

① $8H^+ + 6I^- + 2\overset{+5}{N}O_3^- \longrightarrow 3\overset{0}{I_2} + 2\overset{+2}{N}O + 4H_2O$

$2 \times 3e^- = 6$

$3e \times 2 = 6$

② $1H_2O + 2\overset{+7}{Mn}O_4^- + 1Br^- \longrightarrow 2\overset{+4}{Mn}O_2 + 1\overset{+5}{Br}O_3^- + 2OH^-$

$6e^-$

OWL:
① Acid conditions: balance, adding H_2O's and H^+'s as needed

$2 \times 5 = 10e$

$4H_2O + 2\overset{+5}{Cl}O_3^- + 5\overset{+4}{S}O_2 \longrightarrow 1\overset{0}{Cl_2} + 5\overset{+6}{S}O_4^{2-} + 8H^+$

Os: 6 + 10 20

② ~~Base~~ Acid: end with H_2O's, ~~O~~H^+ as needed (long!!)

$2 \times 3 = 6$

$2H_2O + 2\overset{+7}{Mn}O_4^- + 3\overset{+4}{S}O_2 \longrightarrow 2\overset{+4}{Mn}O_2 + 3\overset{+6}{S}O_4^{2-} + 4H^+$

8 + 6

$3 \times 2 = 6$

4 + 12

Harder balance (OWL): sometimes H_2O, $OH^{\ominus}$, $H^{\oplus}$ omitted, need to be filled in

$\boxed{\text{Handout}}$

Logic

① Balance redox

② Add waters to balance O

③ Add $H^{\oplus}$ to balance H

– if acid conditions, done

④ If "base", add $^{\ominus}OH$'s to cancel $H^{\oplus}$'s

⑤ Cancel H_2O's as needed

19-2

Balancing Oxidation-Reduction Reactions

1. Assign oxidation numbers.

2. Separate into oxidation and reduction half reactions.

3. Balance each half reaction using the following steps:
   a. Balance all elements except oxygen or hydrogen.
   b. Balance oxygen by adding H_2O.
   c. Balance hydrogen by adding H^+.
   d. Balance charge by adding electrons:
      Electrons go on the RIGHT (product side) for OXIDATION reactions.
      Electrons go on the LEFT (reactant side) for REDUCTION reactions.
   e. In BASIC solution, do this additional step:
      For every H^+, add OH^- to BOTH sides of the reaction.
      Combine $H^+ + OH^-$ into H_2O.
      Cancel out any waters that appear on both sides.

   You should now have a balanced half reaction.

4. Multiply balanced half reactions so an equal number of electrons are consumed and produced.

5. Add together half reactions.

6. Clean up. Combine identical substances and reduce coefficients to the lowest terms.

7. CHECK! Atom and charge must balance.

19.3 Electrochemical Cells

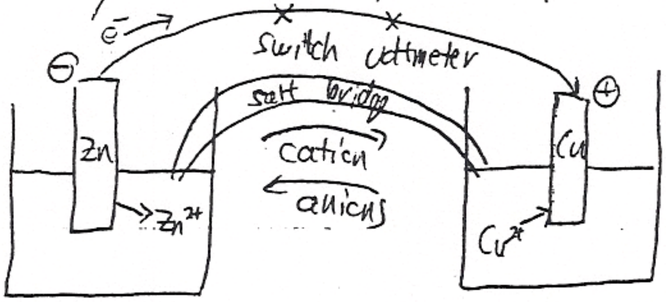
$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ $2e^-$ flow

- when redox partners in contact (same beaker, solution) get direct e^- transfer: no measurable or useful e^- flow

Electrochemical ("Voltaic") Cell: redox reactants <u>separated</u>, so e^- flow forced to go through external circuit ⇒ measurable, useful electricity

<u>Setup</u> (fig 19.5 Moore, Brown 20.5)

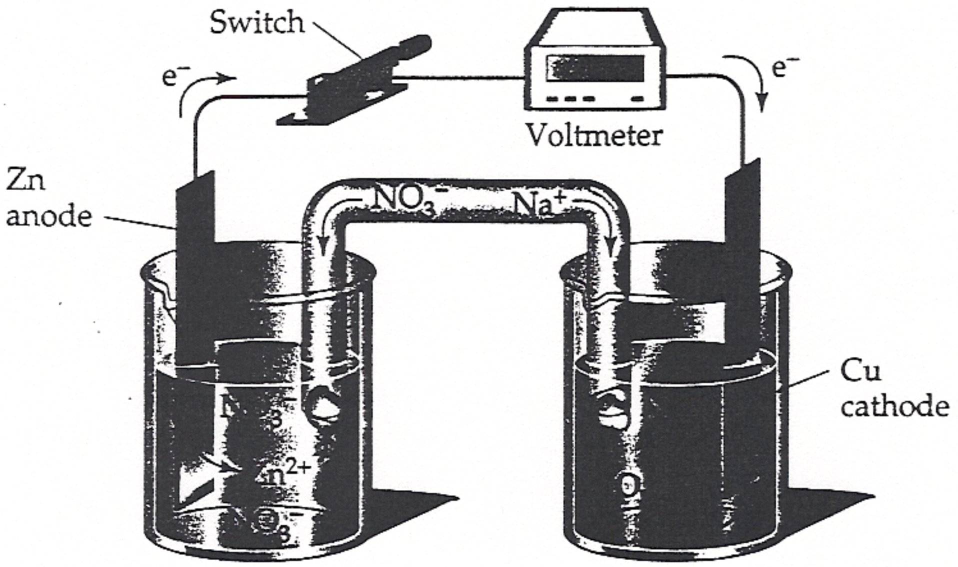
redraw at beginning of class



2 solid metals = "electrodes"
- electrodes can be metal, plates, wires, graphite etc.: (must be conductive)

"<u>A</u>node" = electrode <u>o</u>xidized (vowels) $Zn \rightarrow Zn^{2+}$
- e^- source
- dissolving
- "−" sign on a battery

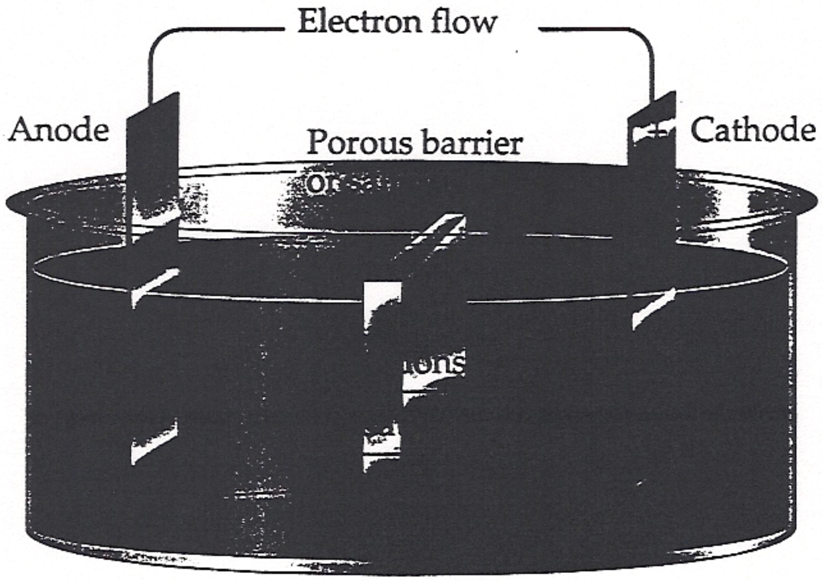
Fig. 20.5 Voltaic Cell
Fig. 20.6 Terminology Used in Describing Voltaic Cell



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

Movement of cations →

← Movement of anions



Anode compartment
Oxidation occurs

Cathode compartment
Reduction occurs

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"Cathode" = " reduced (consonant) $Cu^{2+} \to Cu$

- e^- receiver
- physically electrode grows (Cu° forming)
- "+" sign on battery

2 "Half Cells", "Half Reactions"

Ions must be able to move between halves, in order to maintain charge balance
- use either a "salt bridge" or a "semipermeable membrane" ("porous barrier")

Ion flow: cations move from anode (being produced) to cathode (to replace cations reduced)
Anions move from cathode to anode to balance forming cations

Cell Shorthand Convention:

$$\underbrace{Zn(s) / Zn^{2+}(aq)}_{\text{anode}} // \underbrace{Cu^{2+}(aq) / Cu(s)}_{\text{cathode}}$$

// → barrier between half cells
/ distinction between electrode + ions

Special cells when H_2 gas is produced
(Brown 20.8,

19.4 Electrochemical Cells and Voltage

- depends on redox reactivity, the chemical force for e^- transfer

E_{cell} = cell potential in volts $(V = \frac{1J}{C}$

C = coulomb of electricity

E°_{cell} = <u>standard</u> potential

a) 1.0 M concentration
b) 25°C
c) gases (if any) at 1.0 atm

Since a cell consists of 2 half cells,

$$\boxed{E^\circ_{cell} = \underset{(anode)}{E^\circ_{ox}} + \underset{(cathode)}{E^\circ_{red}}}$$

Each half reaction has an E°, <u>relative</u> to self-defined reference half reaction

$2H^+ + 2e^- \rightarrow H_2 \quad E^\circ = 0$

Show Table 19.1, Cell Handout

ex: $Zn + 2HCl \rightarrow H_2 + ZnCl_2 \quad E^\circ_{cell} = +0.76$

Ox: $Zn \rightarrow Zn^{2+} + 2e^- \quad E_{ox} = ??$

Red: $2H^+ + 2e^- \rightarrow H_2 \quad E_{red} = 0$

$E_{cell} = +.76 = E_{ox} + E_{red} = E_{ox} + 0$ so $\boxed{E_{ox} = +0.76}$

19-5 Using E°_{cell}

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

① Given known halves, deduce E°_{cell}
② Deduce half, given E°_{cell} and other half

③ Tables list <u>reduction</u> halves E°_{red}

④ When a half is reversed, sign reverses
red: $2e^- + Zn^{2+} \rightarrow Zn$ $E^\circ_{red} = -0.76\ V$
ox: $Zn \rightarrow Zn^{2+} + 2e^-$ $E^\circ_{ox} = +0.76$

$$\boxed{E_{ox}^\circ = -E_{red}^\circ}$$

⑤ Stoichiometry coefficients don't matter to E°'s

⑥ For a product-favored reaction, $\boxed{E^\circ_{cell} = \text{positive}}$
– more positive the better

⑦ For half reactions, more positive the more favorable

love of e's
← inverse relationship

red $F_2 \rightarrow 2F^-$ $+2.87$ good!
red $Li^+ \rightarrow Li$ -3.0 bad

ox $Li \rightarrow Li^+$ $+3.0$ good
ox $2F^- \rightarrow F_2$ -2.87 bad

APPENDIX

Standard Reduction (Electrode) Potentials at 25° C

Half-cell reaction	Eo (volts)
$F_2 + 2e \rightarrow 2F^-$	2.87
$Ce^{4+} + e \rightarrow Ce^{3+}$	1.61
$MnO_4^- + 8\,H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$	1.51
$Cl_2 + 2e \rightarrow 2Cl-$	1.36
$Cr_2O_7^{2-} + 14\,H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2 + 4H^+ + 4e \rightarrow 2H_2O$	1.229
$Br_2 + 2e \rightarrow 2Br^-$	1.08
$NO_3- + 4H^+ + 3e \rightarrow NO + 2H_2O$	0.96
$2Hg^{2+} + 2e \rightarrow Hg_2^{2+}$	0.920
$Hg^{2+} + 2e \rightarrow Hg$	0.855
$O_2 + 4\,H^+\ (10^{-7}\,M) + 4e \rightarrow 2H_2O$	0.82
$Ag^+ + e \rightarrow Ag$	0.799
$Hg_2^{2+} + 2e \rightarrow 2Hg$	0.789
$Fe^{3+} + e \rightarrow Fe^{2+}$	0.771
$I_2 + 2e \rightarrow 2I^-$	0.535
$Fe(CN)_6^{3-} + e \rightarrow Fe(CN)_4^{4-}$	0.48
$Cu^{2+} + 2e \rightarrow Cu$	0.337
$Cu^{2+} + e \rightarrow Cu^+$	0.153
$S + 2H^+ + 2e \rightarrow H_2S$	0.14
$2H^+ + 2e \rightarrow H_2$	0.0000
$Pb^{2+} + 2e \rightarrow Pb$	-0.126
$Sn^{2+} + 2e \rightarrow Sn$	-0.14
$Ni^{2+} + 2e \rightarrow Ni$	-0.25
$Co^{2+} + 2e \rightarrow Co$	-0.28
$Cd^{2+} + 2e \rightarrow Cd$	-0.403
$Cr^{3+} + e \rightarrow Cr^{2+}$	-0.41
$2H_2O + 2e \rightarrow H_2 + 2OH^-\ (10^{-7}\,M)$	-0.41
$Fe^{2+} + 2e \rightarrow Fe$	-0.44
$Cr^{3+} + 3e \rightarrow Cr$	-0.74
$Zn^{2+} + 2e \rightarrow Zn$	-0.763
$2H_2O + 2e \rightarrow H_2 + 2OH^-$	-0.83
$Mn^{2+} + 2e \rightarrow Mn$	-1.18
$Al^{3+} + 3e \rightarrow Al$	-1.66
$Mg^{2+} + 2e \rightarrow Mg$	-2.37
$Na^+ + e \rightarrow Na$	-2.714
$K^+ + e \rightarrow K$	-2.925
$Li^+ + e \rightarrow Li$	-3.045

Chapter 19 Electrochemistry Math Summary

Relating Standard Cell Potential to Standard Half Cell Potentials

$E^\circ_{cell}=E^\circ_{oxidation} + E^\circ_{reduction}$ (standard conditions assume 1.0 M concentrations)

Relating Half Cell Potentials when Written in Opposite Directions

$E^\circ_{ox} = -E^\circ_{red}$ for half reactions written in opposite directions

Relating Standard Cell Potentials to ΔG

$\Delta G^\circ = -nFE^\circ_{cell}$ (to give answer in kJ, use F = 96.485)

F = 96,500 C/mol
n=number of electrons transferred

Relating Actual Cell Potential to Standard Cell Potential when Concentrations aren't 1.0-M

$E_{cell} = E^\circ_{cell} -[0.0592/n] \log Q$ (Q = ratio of actual concentrations)

Relating Standard Cell Potential to Equilibrium Constant

$\log K = nE^\circ/0.0592$

Relating Actual Cell Potential to Actual Concentrations in Concentration Cells

$E_{cell} = -[0.0592/n] \log Q$ for concentration cells, where anode and cathode differ only in concentration, but otherwise have same ions

Relating # of Moles of Electrons Transferred as a Function of Time and Current in Electrolysis

1 mol e^- = 96,500 C

moles of electrons = [current (A)•time (sec)]/96,500 for electrolysis, moles, current, and time are related.

rearranged: time (sec)=(moles of electrons)(96500)/current (in A)

Note: 3600 sec/hour

so time (hours)=(moles of electrons)(26.8)/current (in A)

Redox Conjugates: Oxidizing vs. Reducing Agents

① On table, left side = oxidizing agents
right side = reducing agents

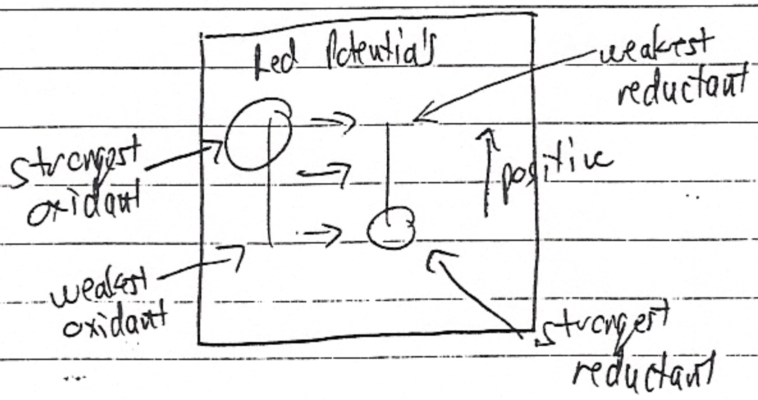
oxidized form ⇒ $\underset{\text{oxidant}}{F_2} + 2e^- \longrightarrow 2\underset{\text{reductant}}{F^-}$ ⇐ reduced form

② In oxidized form: higher E°_{red} ⇒
a) more easily reduced
b) stronger love for e's
c) stronger oxidizing agent

③ In conjugate reduced form:
- lower on chart means oxidation will be more positive!!
- lower on chart means lower love for e's (if love, ox. form want to be reduced
red form wants to hold

Brown Fig 20.10

Strongest oxidizing agent: top left (max e^- love
Strongest reducing agent: bottom right (min e^- love,



top: max e^- love

bottom: min e^- love

Odds n Ends

① An oxidizing agent on table will react (product-favored) with any reducing agent lower
- will not react with any reducing agent higher (reactant favored)

② For two species to react one must be in reduced form (reducing agent), other in oxidized form (oxidizing agent)

③ Given chart, rank e^- love and predict anything.

*④ Based on periodic table, predict reactivity without table

~~Reduced form~~

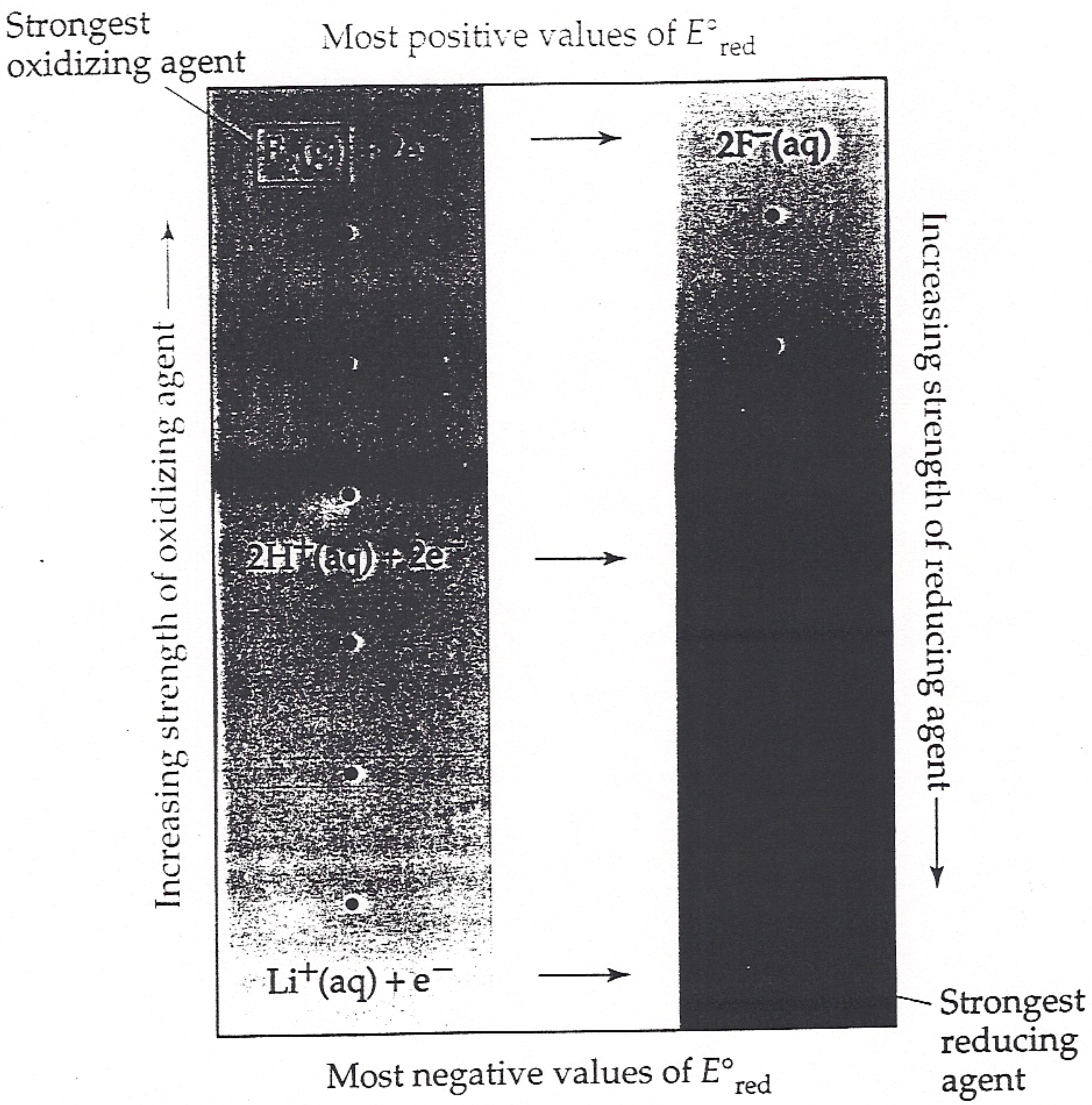
Activity (as reducing agents, increasing e^- love)

$\underbrace{G1 > G2}_{\text{active metals}} > Al > \text{most T-metals} > H_2 > \text{coinage metals}$

ex: Li Mg Al Ni H_2 Cu

⑤ Given 2 redn. potentials, figure out how a product-favored cell would be constructed
- Keep better as redn, reverse the other to ox
- then sum $E^\circ_{red} + E^\circ_{ox}$ to get E°_{cell}

Fig. 20.10 Oxidizing/Reducing Agents



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(19-11)

$Fe^{3+} \rightarrow Fe^{2+}$	+.77 V
$Cu^{2+} \rightarrow Cu$	+.34 V
$2H^+ \rightarrow H_2$	0
$Pb^{2+} \rightarrow Pb$	−.13
$Ni^{2+} \rightarrow Ni$	−.25
$Cr^{3+} \rightarrow Cr^{2+}$	−.74

① $Ni + Fe^{3+} \longrightarrow Fe^{2+} + Ni^{2+}$ Balance, and find E°_{cell}

② $Sn + Cu^{2+} \longrightarrow Cu + Sn^{2+}$ $E^\circ_{cell} = +0.48\ V$

Find E°_{ox} for $Sn \rightarrow Sn^{2+}$,
E°_{red} for $Sn^{2+} \rightarrow Sn$

③ Rank the oxidizing agents by strength

④ Rank the reducing agents by strength

⑤ which will react with Cu^{2+}?

⑥ " Cu°?

$Fe^{3+} \rightarrow Fe^{2+}$	+.77 V
$Cu^{2+} \rightarrow Cu$	+.34 V
$2H^+ \rightarrow H_2$	0
$Pb^{2+} \rightarrow Pb$	−.13
$Ni^{2+} \rightarrow Ni$	−.25
$Cr^{3+} \rightarrow Cr^{2+}$	−.74

① $1Ni + 2Fe^{3+} \longrightarrow 2Fe^{2+} + 1Ni^{2+}$ Balance, and find E°_{cell}

$E = \underset{red}{.77} + \underset{ox}{.25} = \boxed{1.02\,V}$

↑ reverse sign

② $Sn + Cu^{2+} \longrightarrow Cu + Sn^{2+}$ $E^{\circ}_{cell} = +0.48\,V$

+.34 red

$.48 = .34 + E_{ox}$

$E_{ox} = +.14\,V$

Find E°_{ox} for $Sn \rightarrow Sn^{2+}$, $\boxed{+.14}$

E°_{red} for $Sn^{2+} \rightarrow Sn$ $\boxed{-.14}$

③ Rank the oxidizing agents by strength

$Fe^{3+} > Cu^{2+} > H^+ > Pb^{2+} > Ni^{2+} > Cr^{3+}$

$\boxed{\text{left side, top down}}$

④ Rank the reducing agents by strength

$Cr^{2+} > Ni > Pb > H_2 > Cu > Fe^{2+}$

$\boxed{\text{right side, bottom up}}$

⑤ which will react with Cu^{2+}?

reducing agents (right) + <u>lower</u> H_2, Pb, Ni, Cr^{2+}

⑥ Cu°? Fe^{3+}

oxidizing agent (left) + <u>higher</u>

19-13

⑥ If $X + Y^{2+} \longrightarrow Y + X^{2+}$ Reaction Happens

Then Activity $X > Y$ as reducing agents
$X^{2+} < Y^{2+}$ oxidizing agents
Y loves e's more than X

$\boxed{\text{Reaction favors "weaker" side}}$

If $X + Z^{2+} \not\longrightarrow X^{2+} + Z$ No Reaction

Then $X < Z$ as reducing agent
$Z^{2+} < X^{2+}$ as oxidizing agent
X loves e's more than Z

(9-14)

① $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$ $E^\circ = 0.32\ V$

What is the "reduction potential for Fe^{2+} ($Fe^{2+} \rightarrow Fe$
given the above potential, and given that
$Zn^{2+} \rightarrow Zn$ $E^\circ_{red} = -0.76$.

② Find E° for product favored reaction involving the following, and balance the reaction.

$Fe^{3+} \rightarrow Fe^{2+}$ 0.77
$Cu^{2+} \rightarrow Cu$ 0.34

a. keep more favorable one as reduction
b. reverse less favorable to make it an oxidation
c. Sum E°_{ox} and E°_{red}
d. adjust coefficients to balance e's

③ Ditto for $Br_2 \rightarrow 2Br^-$ +1.06
$Zn^{2+} \rightarrow Zn$ −0.76

(9-14)

① $Zn + Fe^{2+} \longrightarrow Zn^{2+} + Fe \qquad E^\circ = 0.32\,V$

ox = +.76

What is the "reduction potential for Fe^{2+} ($Fe^{2+} \rightarrow Fe$
given the above potential, and given that
$Zn^{2+} \rightarrow Zn \quad E^\circ_{red} = -0.76$.

$.32 = E_{red} + .76$

$\boxed{E_{red} = -0.44\,V}$

② Find E° for product favored reaction
involving the following, and balance the reaction.

$Fe^{3+} \rightarrow Fe^{2+} \quad 0.77$
$Cu^{2+} \rightarrow Cu \quad 0.34$

a. keep more favorable one as reduction
b. reverse less favorable to make it an oxidation
c. Sum E°_{ox} and E°_{red}
d. adjust coefficients to balance e's

$2Fe^{3+} + 1Cu \longrightarrow 2Fe^{2+} + 1Cu^{2+}$

$+.77 \qquad -.34 \quad = \boxed{+.43\,V}$

③ Ditto for $Br_2 \rightarrow 2Br^- \quad +1.06$
$Zn^{2+} \rightarrow Zn \quad -0.76$

$1Br_2 + 1Zn \longrightarrow 2Br^- + 1Zn^{2+}$

$+1.06 \qquad +.76 \quad = \boxed{1.82\,V}$

(19-15)

① Predict/Rank E_{ox}° for

Li Mg Fe H_2 Ag

② Rank/Predict E_{red}° for

Li^+ Mg^{2+} Fe^{2+} H^+ Ag^+

③ Rank F_2 Cl_2 I_2 as oxidizing agents

④ $F^{\ominus}$ $Cl^{\ominus}$ $I^{\ominus}$ as reducing agents

⑤ Reduction potentials for Ni^{2+} and Sn^{2+} are −0.25V and −0.16 V.

a. Which of Ni^{2+} and Sn^{2+} is stronger oxidizing agent?

b. Which of Ni and Sn is stronger reducing agent?

c. Which of Ni and Sn would react with H^+?

19-15

① Predict/Rank E°_{ox} for

$\underset{G1}{Li} > \underset{G2}{Mg} > \underset{T\text{-met}}{Fe} > \underset{H_2}{H_2} > \underset{\text{Coinage}}{Ag}$

② Rank/Predict E°_{red} for

$Li^+ < Mg^{2+} < Fe^{2+} < H^+ < Ag^+$

$\xrightarrow{\text{love for e's}}$

③ Rank $F_2 > Cl_2 > I_2$ as oxidizing agents

e^- love

↓

$F^\ominus$

④ $F^\ominus < Cl^\ominus < I^\ominus$ as reducing agents

max love, highest hetention

min love, most willing to release

⑤ Reduction potentials for Ni^{2+} and Sn^{2+} are $-0.25V$ and $-0.16 V$.

$2H^+ \longrightarrow H_2$ 0

$Sn^{2+} \longrightarrow Sn$ $-.16$

$Ni^{2+} \longrightarrow Ni$ $-.25$

a. Which of Ni^{2+} and Sn^{2+} is stronger <u>oxidizing</u> agent? $\boxed{Sn^{2+}}$

b. Which of Ni and Sn is stronger <u>reducing</u> agent? $\boxed{Ni}$

c. Which of Ni and Sn would react with H^+? $\boxed{\text{Both}}$

Activity $\bar{e}$ love (19-16)

① $3A + 2B^{3+} \rightarrow 2B + 3A^{2+}$

$B + C^{2+} \rightarrow C + D^{2+}$

$A + D^{2+} \rightarrow$ No Reaction

Rank activity of A, B, C, D

Rank activity of A^{2+}, B^{3+}, C^{2+}, D^{2+}

Rank $\bar{e}$ love:

	V
$Ag^+ \rightarrow Ag$	+0.80
$Cu^{2+} \rightarrow Cu$	+0.34
$Zn^{2+} \rightarrow Zn$	−0.76
$Al^{3+} \rightarrow Al$	−1.66
$Mg^{2+} \rightarrow Mg$	−2.36

② Which species react with Cu^{2+}?

③ Which react with Zn^0?

④ Which element loves e's most? Least?

⑤ $NiCl_2 + H_2 \rightarrow Ni + 2HCl$ $E^\circ = -0.28V$

a. Product favored?

b. Is reduction potential for Ni^{2+} positive?

(19-16)

	Activity	$\bar{e}$ love
① $3A + 2B^{3+} \longrightarrow 2B + 3A^{2+}$	$A > B$	$B > A$
$B + C^{2+} \longrightarrow C + B^{2+}$	$B > C$	$C > B$
$A + D^{2+} \longrightarrow$ No Reaction	$A < D$ or $D > A$	$A > D$

Rank activity of A, B, C, D $D > A > B > C$

Rank activity of $A^{2+}, B^{3+}, C^{2+}, D^{2+}$

$D^{2+} < A^{2+} < B^{3+} < C^{2+}$

Rank $\bar{e}$ love:

$C^{2+} \rightarrow C$
$B^{3+} \rightarrow B$
$A^{2+} \rightarrow A$
$D^{2+} \rightarrow D$

- - - - - -

		$\vee$
$Ag^+ \longrightarrow Ag$		$+0.80$
$Cu^{2+} \longrightarrow Cu$		$+0.34$
$Zn^{2+} \longrightarrow Zn$		-0.76
$Al^{3+} \longrightarrow Al$		-1.66
$Mg^{2+} \longrightarrow Mg$		-2.36

② Which species react with Cu^{2+}? $\boxed{\text{lower left}}$ reducing agents

Zn, Al, Mg

③ Which react with Zn^0? $\boxed{\text{upper right}}$ oxidizing agents

Ag^+, Cu^{2+}

④ Which element loves e's most? Least?

Mg   Ag

⑤ $NiCl_2 + H_2 \longrightarrow Ni + 2HCl$ $E^\circ = -0.28V$

a. Product favored? $\boxed{\text{No!}}$ E° <u>positive for</u> prod favored

b. Is reduction potential for Ni^{2+} positive?

$\boxed{\text{No!}}$ $H_2 \rightleftarrows 2H^+$ 0V

19.6 E° and ΔG°

	ΔG	E°	K
Product favored	neg	pos	large
Reactant Favored	pos	neg	small
*Equilibrium	0	0	1

ΔG°, E° have opposite signs, but related!!
K also

$$\boxed{\Delta G^\circ = -nFE^\circ}$$

n = # of electrons transferred in equation
(now coefficients matter!

F = Faraday's constant
= $\boxed{96.5}$ to get ΔG in kJ/mol

Units: $F = \frac{96\,500\ C}{mol\ e^-}$ $V = \frac{J}{C}$ so $\frac{C}{mol\ e^-}\left(\frac{J}{C}\right) = \frac{J}{mol}$

"C = coulomb, unit of electricity"
"free energy to do the work of moving e's"

Likewise voltage and K linked:

$$\boxed{\log K = nE^\circ/(.0592)}$$

(19-18)

① $Cu + Fe^{3+} \longrightarrow Cu^{2+} + Fe^{2+}$

$+0.77\,V$ $\quad +0.34\,V$

Balance the reaction, and find ΔG° given the reduction potentials shown.

② $Zn + Cr^{3+} \longrightarrow Zn^{2+} + Cr \quad \Delta G^\circ = -11.6\,\frac{kJ}{mol}$

a. Balance the reaction, and calculate E°.

b. If the reduction potential for Zn^{2+} is $-0.76\,V$, what is the reduction potential for Cr^{3+}?

③ $Ag^{+} + Fe^{2+} \rightleftharpoons Ag^{0} + Fe^{3+}$

$+0.80\,V$ $\quad +0.77\,V$

Calculate K, given reduction potentials.

(19-18)

① $1Cu + 2Fe^{3+} \longrightarrow 1Cu^{2+} + 2Fe^{2+}$

$+0.77V \quad +0.34V \qquad n=2$

Balance the reaction, and find ΔG° given the reduction potentials shown.

$\Delta G = -n(96.5)E^\circ \qquad n=2 \quad E^\circ = .77 - .34 = +.43V$

$= -2(96.5)(.43)$

$\boxed{\Delta G = -83 \text{ kJ/mol}}$

① balance, find n
② work out E°
③ plug + chug

$2e \times 3 = 6$

② $3Zn + 2Cr^{3+} \longrightarrow 3Zn^{2+} + 2Cr \quad \Delta G^\circ = -11.6 \frac{kJ}{mol}$

$3e \times 2 = 6$

a. Balance the reaction, and calculate E°.

$-11.6 = -6(96.5)(E^\circ)$

$\boxed{E^\circ = +0.02 \text{ V}}$

b. If the reduction potential for Zn^{2+} is $-0.76V$, what is the reduction potential for Cr^{3+}?

$.02 = \text{red} + .76 \qquad \boxed{E_{red} = -0.74}$

③ $Ag^+ + Fe^{2+} \rightleftharpoons Ag^0 + Fe^{3+}$

$+0.80V \qquad +0.77V$

$+.80 \qquad -.77$

Calculate K, given reduction potentials.

① balance, find n
② work out E°

$\log K = \frac{nE^\circ}{.0592} = \frac{.03}{.0592} = 0.507 \qquad K = 10^{.507}$

$n=1$
$E^\circ = +.03$

$\boxed{K = 3.21}$

19.7 Effect of Concentration on Cell Potential

- E° assumes 1.0 M concentrations
- rarely true!
- ★ for any reaction, concentrations change and voltage drops until battery is dead = 0V = equilibrium

Nernst Eqn: $\boxed{E_{actual} = E^\circ - \frac{.0592}{n} \log Q}$

n = # of e's transferred (need balanced eq. coefficients)

Q = ratio of actual concentrations, K format

- recall solids, liquids don't appear

[Note: At eq: $E=0$ $Q=K$

so $0 = E^\circ - \frac{.0592}{n} \log K$

$E^\circ = \frac{.0592}{n} \log K$]

"Concentration cells": anode/cathode use the same things, but with ions at diff conc.

ex: $H_2 + 2H^+ \rightleftharpoons H_2 + 2H^+$ $E^\circ = 0$

so $E_{actual} = -\frac{.0592}{n} \log Q$

- the voltage is key to pH meters, neurons (19.8) (concs inside/out cell membrane)

(19-20)

① Calculate actual voltage for
$Mg / Mg^{2+}(0.10\,M) // Cu^{2+}(0.001\,M) / Cu$
given the following reduction potentials:

Mg^{2+} −2.37 V

Cu^{2+} +0.34 V

Logic Steps

② Same for $Cu/Cu^{2+}(1.0\,M) // Ag^{+}(0.032\,M) / Ag$

E°_{red}

Ag^{+} +0.80 V

Cu^{2+} +0.34 V

③ $2\,Ag^{+}(aq) + Zn(s) \longrightarrow 2\,Ag(s) + Zn^{2+}(aq)$

E^{0}_{red} +0.80 −0.76

If a cell with $[Ag^{+}] = 0.20\,M$ has $E_{actual} = 1.63\,V$,
what is $[Zn^{2+}]$?

19-20

① Calculate actual voltage for
$Mg \,/\, Mg^{2+}(0.10\,M) \,//\, Cu^{2+}(0.001\,M) \,/\, Cu$

given the following reduction potentials:

Mg^{2+} -2.37 V
Cu^{2+} $+0.34$ V

Logic Steps
① write reaction
② Balance reaction
③ Find $n \Rightarrow 2$
④ Find $E^\circ \Rightarrow +2.71V$
⑤ Enter 'Q'

$1Mg + 1Cu^{2+} \longrightarrow Mg^{2+} + 1Cu$

$+2.37 \qquad +.34 \quad = +2.71$

$$E = E^\circ - \frac{.0592}{n}\log Q$$

$$= 2.71 - \frac{.0592}{2}\log\left(\frac{.10}{.001}\right) = \boxed{2.65\ V}$$

② Same for $Cu/Cu^{2+}(1.0\,M) \,//\, Ag^+(0.032\,M)/Ag$

$\underline{E_{red}^\circ}$
Ag^+ $+0.80V$
Cu^{2+} $+0.34V$

$1Cu + 2Ag^+ \longrightarrow 1Cu^{2+} + Ag \qquad n=2$

$-.34 \quad .80 = +.46V$

$$E = .46V - \frac{.0592}{2}\log\frac{1}{(.032)^2} = \boxed{[illegible]}\ \boxed{+0.37V}$$

③ $2Ag^+(aq) + Zn(s) \longrightarrow 2Ag(s) + Zn^{2+}(aq) \qquad n=2$

E_{red}^0 $+0.80$ $\qquad -0.76 \qquad E^0 = 1.56V$

If a cell with $[Ag^+] = 0.20M$ has $E_{actual} = 1.63V$, what is $[Zn^{2+}]$?

$$1.63 = 1.56 - \frac{.0592}{2}\log\frac{[Zn^{2+}]}{(.20)^2}$$

$$.07 = -\frac{.0592}{2}\log(\ )$$

$$-2.36 = \log\frac{[Zn^{2+}]}{(.20)^2}$$

$$.00432 = \frac{[Zn^{2+}]}{(.20)^2}$$

$$\boxed{[Zn^{2+}] = 1.73\times10^{-4}}$$

(19-21)

19.9 Common Batteries

A. Primary ("Dry Cell"): Nonrechargeable
- run till concentrations achieve equilibrium, ≡ dead ⇒ toss

① alkaline batteries

$$H_2O + \underset{\substack{\text{anode}\\ \text{oxidized}}}{Zn(s)} + \underset{\substack{\text{cathode}\\ \text{reduced}}}{MnO_2(s)} \longrightarrow ZnO(aq) + 2MnO(OH)($$

- reduction at a graphite electrode

$E^\circ = 1.54$ V

- flashlights, radio, toys, etc.

② mercury battery $Zn + HgO \rightarrow ZnO + Hg$

$E^\circ = 1.35$ V, but smaller

- used in small things (calculators, watches, cameras --)
- mercury is poisonous, environmental issue

B.

B. Secondary Batteries ("nicad" and "car") Rechargeable

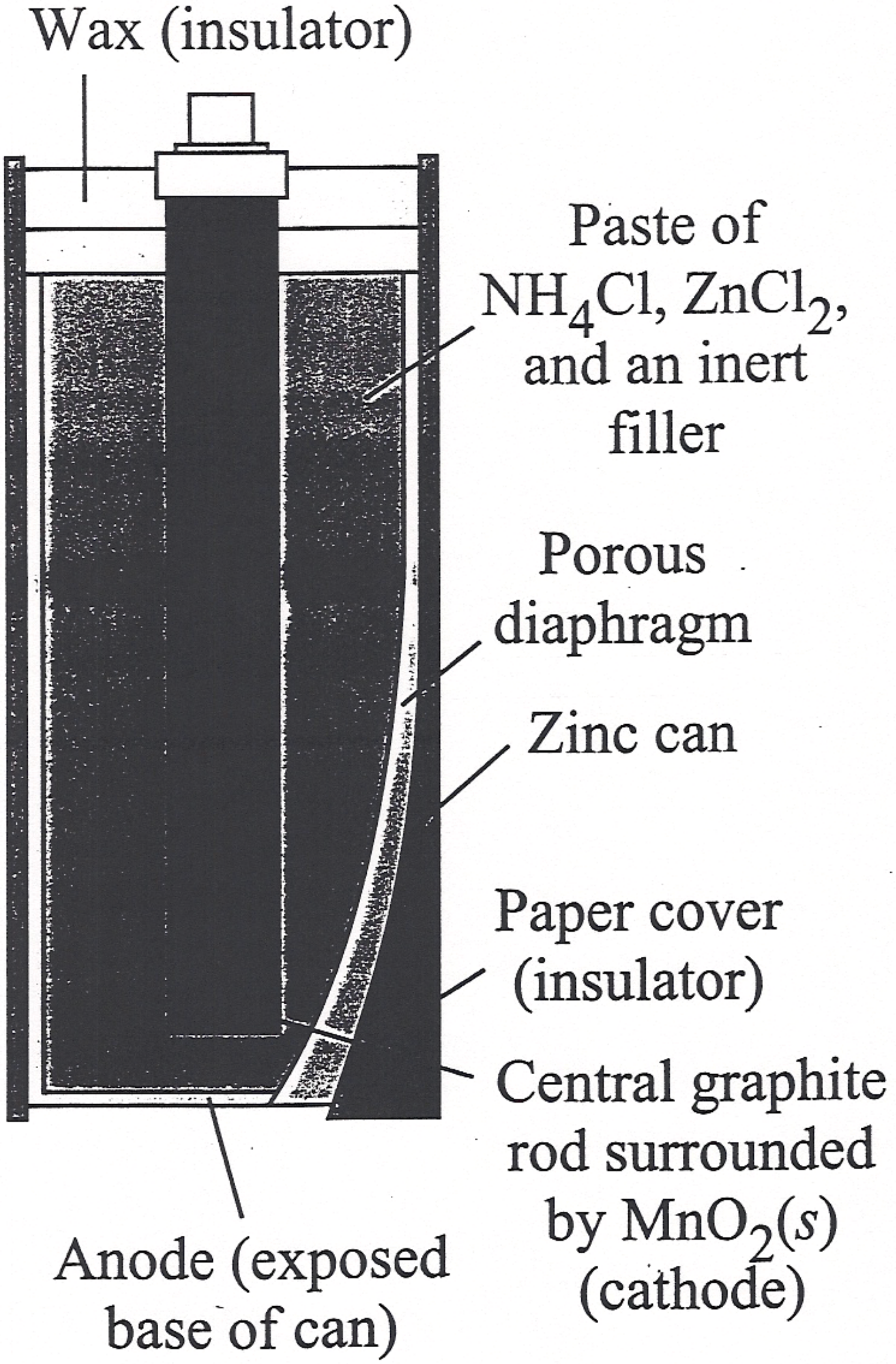
① Lead-acid (car battery)

$$\underset{\text{anode}}{Pb^0(s)} + \underset{\text{cathode}}{\overset{+4}{Pb}O_2(s)} + \underset{\substack{\uparrow\\ \text{careful!!}}}{2H_2SO_4} \longrightarrow 2PbSO_4(s) + 2H_2O$$

leakage caused corrosion

$E^\circ = 2.0$ V

T 93 Fig. 13.6 The Dry Cell



ATOMS MOLECULES
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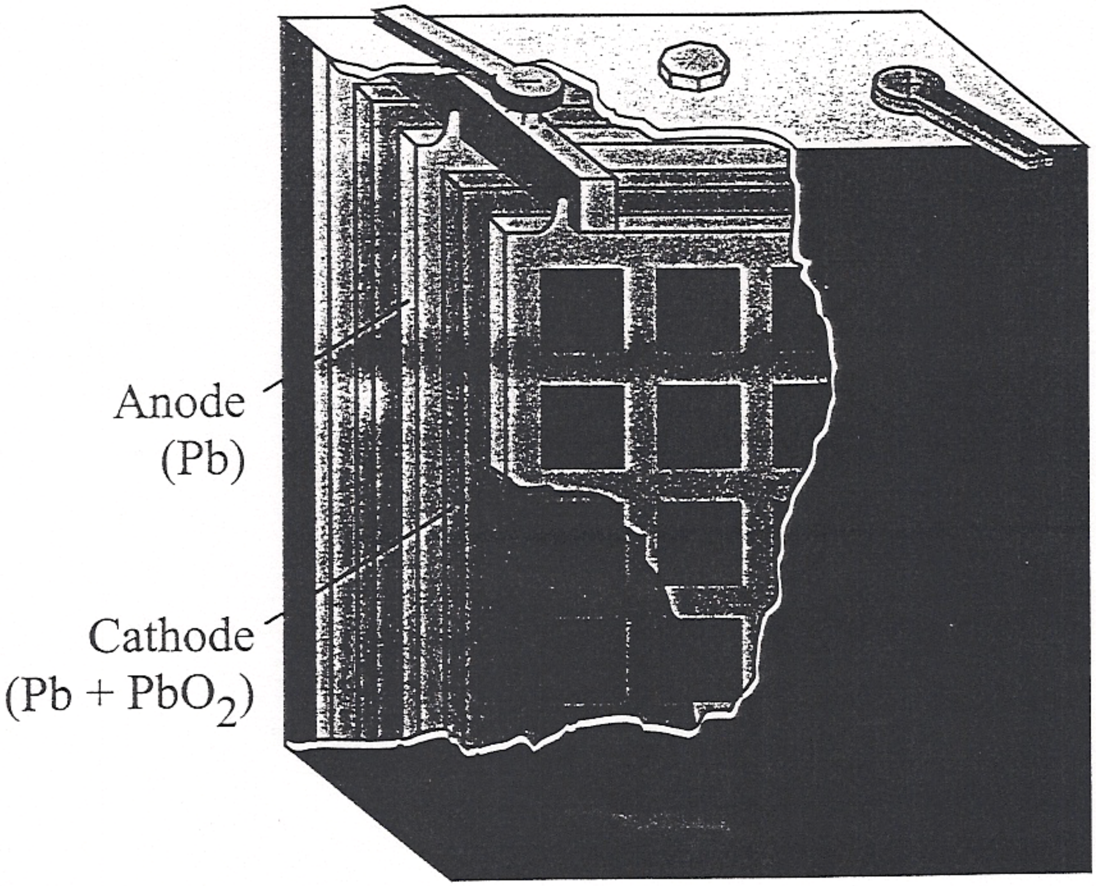
T 94 Fig. 13.7 A Lead-Acid Cell



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19-22

- the $PbSO_4(s)$ stays on electrodes, so reaction can be reversed when "recharged"
- each cell is 2.0 V: six alternating cathodes/anodes in series sums to 12 V.
- side products during recharge:

ox: $6H_2O \rightarrow \boxed{O_2} + 4H_3O^{\oplus} + 4e^-$

red: $4H_2O + 4e^- \rightarrow 2\boxed{H_2} + 4OH^-$

explosive, no sparks!!

② Nicad $E^0 = 1.3$

- electric shavers, toothbrushes, video camcorders

any rechargeable cordless appliance

$\overset{0}{Cd}(s) + 2\overset{+3}{Ni}\overset{(OH)}{O_2}(s) + 2H_2O \rightleftharpoons \overset{+2}{Cd}(OH)_2(s) + 2\overset{+2}{Ni}(OH)_2(s)$

anode cathode $E^0 = 1.3$

- again, solid products stay, can reverse

③ Li $Li(s) + CoO_2(s) \longrightarrow LiCoO_2(s)$ $E^0 = 3.4V$

(in polymer with carbon) graphite

- more expensive

Pros: ① light weight

② big voltage ⇒ energy eaters

laptops, cameras, cell phones

(19-23)

19.10 Fuel Cell: continuous feed of reactants from outside to electrodes

$2H_2 + O_2 \longrightarrow 2H_2O \quad E^\circ = 0.9\,V$

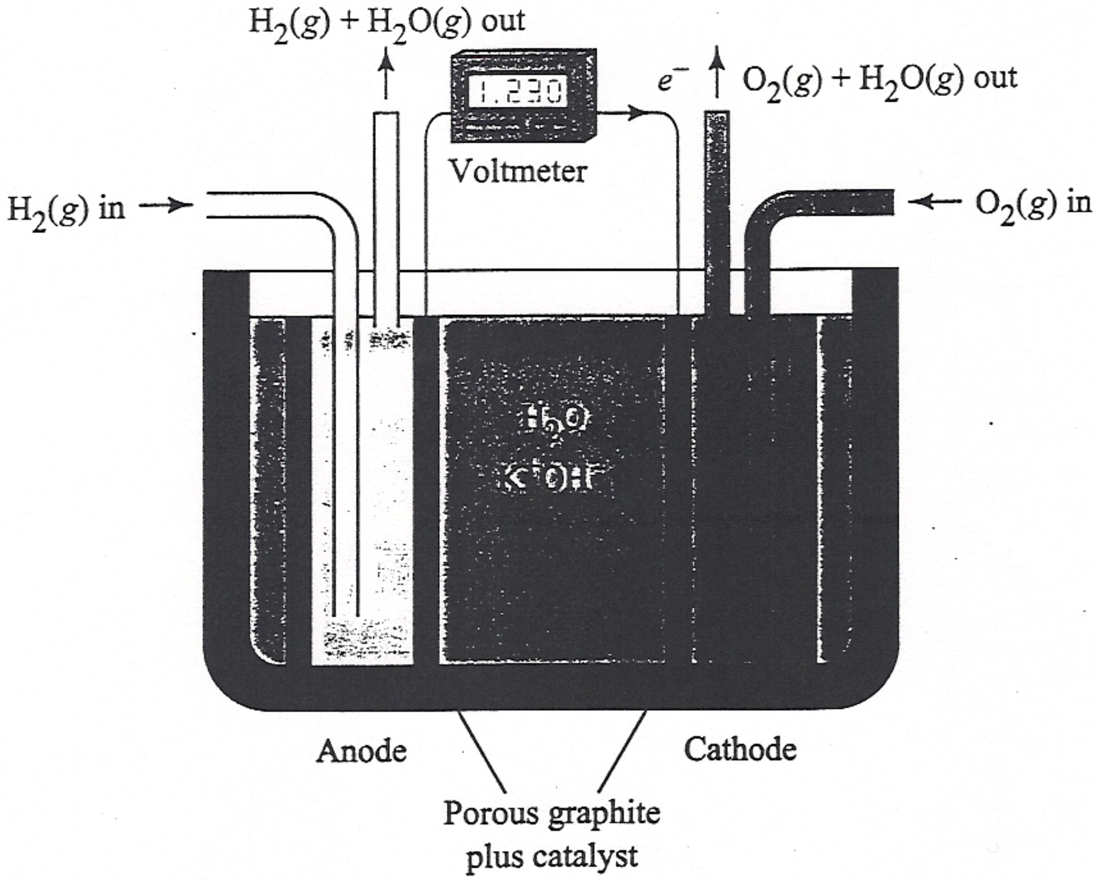
$\underset{anode}{}$ anode   cathode

- H_2 + O_2 light, so good fuels, high energy effici
  - spaceship 500 lb fuel ⇒ 11 days

Dream: way to use solar/wind energy to produce H_2 → get H_2O, pollution free

Fuel cells future for cars??

T 95 Fig. 13.8 Fuel Cell



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19.11 Electrolysis: Using outside electrolysis to force unfavorable redox to go to product side
- Key route to elements not found in nature: metals, H_2, Cl_2 ...

A. Electrolysis of Molten Salts
↳ melted, pure (hot!)

ex: $2\overset{e^-}{Na}\overset{e^-}{Cl} \longrightarrow 2Na + Cl_2$ $E^0 = -4.07$ V

Cathode, e^- acceptor ↗ (Na)   anode, e source ↑ (Cl)

(Brown, Gillespie overheads)

- products must be kept separate so can't react

B. Electrolysis of salts in Water
- at electrodes, the [illegible] most reactive candidate reacts ⇒ in water, can only ~~reduce cations~~ process ions more reactive than water

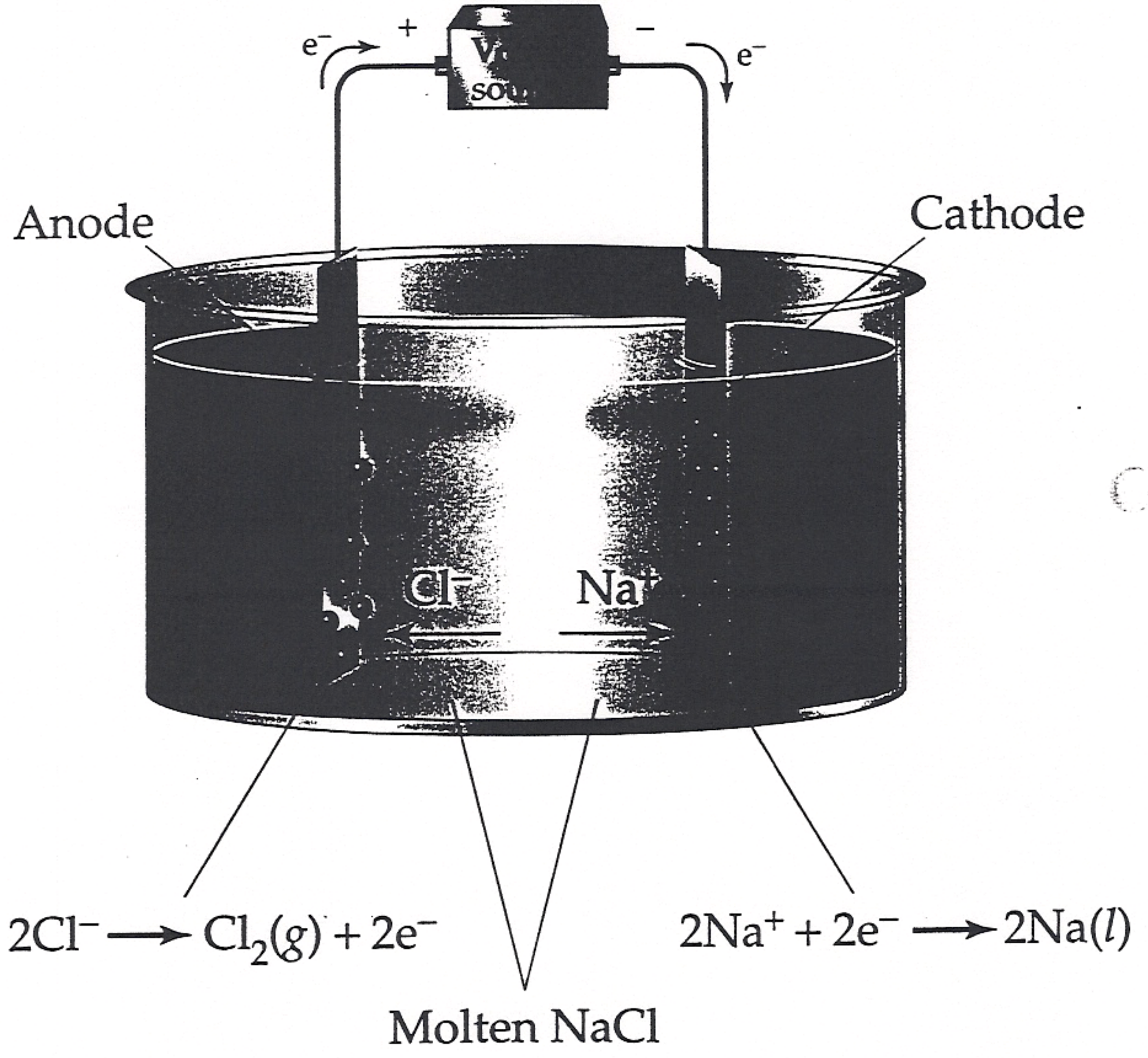
water reduction: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ $E^0 = -.83$

oxidation $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$ $E^0 = -1.23$

Easily reduced cations (Zn^{2+}, Ni^{2+}, Cr^{3+}, Sn^{2+}, etc.) can be reduced in water

Cations of Active metals can't (K^+, Mg^{2+}, Na^+ ...)

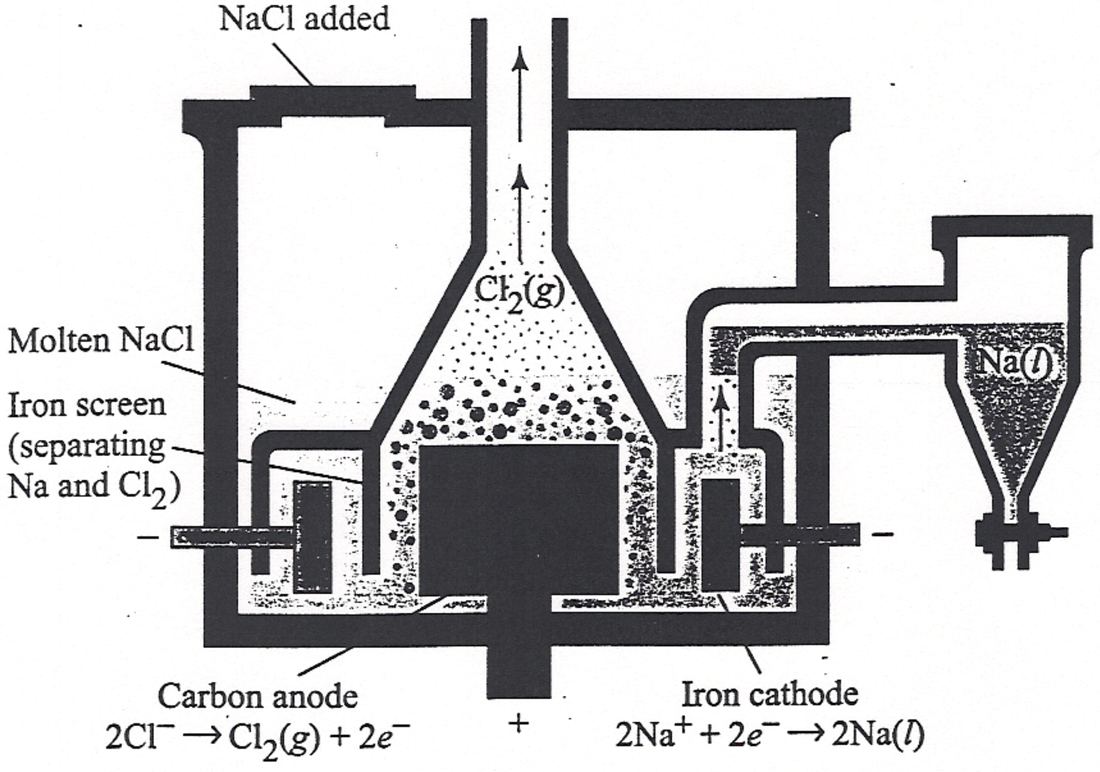
Fig. 20.19 Electrolysis of NaCl



CHEMISTRY: The Central Science 7/e
by Brown/Lemay/Bursten

Simon & Schuster/A Viacom Company
Upper Saddle River, NJ 07458

T 99 Fig. 13.13 Electrolytic Cell for the Commercial Production of Sodium



ATOMS MOLECULES
AND REACTIONS
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APPENDIX
Standard Reduction (Electrode) Potentials at 25° C

Half-cell reaction	**Eo (volts)**	
$F_2 + 2e \rightarrow 2F^-$	2.87	
$Ce^{4+} + e \rightarrow Ce^{3+}$	1.61	
$MnO_4^- + 8 H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$	1.51	
$Cl_2 + 2e \rightarrow 2Cl-$	1.36	
$Cr_2O_7^{2-} + 14 H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$	1.33	
$O_2 + 4H^+ + 4e \rightarrow 2H_2O$	1.229	
$Br_2 + 2e \rightarrow 2Br^-$	1.08	
$NO_3- + 4H^+ + 3e \rightarrow NO + 2H_2O$	0.96	
$2Hg^{2+} + 2e \rightarrow Hg_2^{2+}$	0.920	
$Hg^{2+} + 2e \rightarrow Hg$	0.855	
$O_2 + 4 H^+ (10^{-7} M) + 4e \rightarrow 2H_2O$	0.82	oxidation of water
$Ag^+ + e \rightarrow Ag$	0.799	
$Hg_2^{2+} + 2e \rightarrow 2Hg$	0.789	
$Fe^{3+} + e \rightarrow Fe^{2+}$	0.771	
$I_2 + 2e \rightarrow 2I^-$	0.535	
$Fe(CN)_6^{3-} + e \rightarrow Fe(CN)_4^{4-}$	0.48	
$Cu^{2+} + 2e \rightarrow Cu$	0.337	
$Cu^{2+} + e \rightarrow Cu^+$	0.153	
$S + 2H^+ + 2e \rightarrow H_2S$	0.14	
$2H^+ + 2e \rightarrow H_2$	0.0000	
$Pb^{2+} + 2e \rightarrow Pb$	-0.126	
$Sn^{2+} + 2e \rightarrow Sn$	-0.14	
$Ni^{2+} + 2e \rightarrow Ni$	-0.25	
$Co^{2+} + 2e \rightarrow Co$	-0.28	
$Cd^{2+} + 2e \rightarrow Cd$	-0.403	
$Cr^{3+} + e \rightarrow Cr^{2+}$	-0.41	
$2H_2O + 2e \rightarrow H_2 + 2OH^- (10^{-7} M)$	-0.41	reduction of water
$Fe^{2+} + 2e \rightarrow Fe$	-0.44	
$Cr^{3+} + 3e \rightarrow Cr$	-0.74	
$Zn^{2+} + 2e \rightarrow Zn$	-0.763	→
$2H_2O + 2e \rightarrow H_2 + 2OH^-$	-0.83	
$Mn^{2+} + 2e \rightarrow Mn$	-1.18	
$Al^{3+} + 3e \rightarrow Al$	-1.66	
$Mg^{2+} + 2e \rightarrow Mg$	-2.37	
$Na^+ + e \rightarrow Na$	-2.714	
$K^+ + e \rightarrow K$	-2.925	
$Li^+ + e \rightarrow Li$	-3.045	

(19-25)

Electroplating: $M^+ \longrightarrow M$

- metal forms on surface of cathode
- many metals are "plated" on outside of things in this way
  - Cl_2, NaOH made by electrolysis

19.12 Electrolysis Calculations

$$\boxed{1 \text{ mol } e^-\text{'s} = 96{,}500 \text{ C}}$$

$$A \text{ (amp)} = \frac{C}{\text{sec}}$$

Current, time, moles e^- related!

$$\boxed{\text{moles } e^- = \frac{\text{current (A)} \cdot \text{sec}}{96500}}$$

$$\boxed{\text{sec} = \frac{(\text{moles})\, 96500}{A}}$$

Relationships

$$\boxed{\text{current } A + \text{time}} \longleftrightarrow \boxed{\text{Moles of } e^-} \longleftrightarrow \boxed{\text{Moles of Substance -Reduced}} \longleftrightarrow \boxed{\text{Grams of Substance}}$$

(19-26)

① How many grams of Al (27g/mol) is produced in 1.0 h by electrolysis of $AlCl_3$ at 10.0 A current?

② At 3.2 A, how long will it take to make 10g of Zn (65.4g/mol) from $ZnBr_2$?

③ What metals could be formed at [redacted] cathode in water?

$Hg^{2+} \rightarrow Hg$	0.9 V
$Cu^{2+} \rightarrow Cu$	0.2 V
$Co^{2+} \rightarrow Co$	−0.3 V
$2H_2O \rightarrow H_2 + 2OH^-$	−0.4 V
$Mn^{2+} \rightarrow Mn$	−1.2 V
$Mg^{2+} \rightarrow Mg$	−2.4 V

(19-26)

① How many grams of Al (27g/mol) is produced in 1.0 h by electrolysis of $AlCl_3$ at 10.0 A current?

① moles of e^-

② moles of e^- per mole of Al

③ mol → g Al

★ change time to sec

$x \text{ mol } e^- = \frac{(10\,A)(1\,h)}{96500}\left(\frac{60\,min}{1\,h}\right)\left(\frac{60\,s}{1\,min}\right) = 0.373 \text{ mol } e^-$

$3e^- + Al^{3+} \rightarrow Al$

$x \text{ mol Al} = \frac{.373 \text{ mol } e^-}{} \Big| \frac{1 \text{ mol Al}}{3 \text{ mol } e^-}$

$= \frac{0.124 \text{ mol Al}}{} \Big| \frac{27\,g}{1 \text{ mol Al}}$

$= \boxed{3.36\,g \text{ Al}}$

② At 3.2 A, how long will it take to make 10g of Zn (65.4g/mol) from $ZnBr_2$?

$s = \frac{mol \cdot 96500C}{A}$

$x \text{ mol } e^- = \frac{10g \text{ Zn}}{} \Big| \frac{1 \text{ mol Zn}}{65.4g} \Big| \frac{2 \text{ mol } e^-}{1 \text{ mol Zn}}$

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

$= 0.306 \text{ mol } e^-$

$= \frac{(.306)(96500)}{3.2}$

$= \frac{9228 \text{ sec}}{} \Big| \frac{1 \text{ min}}{60 \text{ sec}} \Big| \frac{1\,h}{60 \text{ min}} = \boxed{2.56 \text{ hours}}$

③

$Hg^{2+} \rightarrow Hg$ 0.9 V

$Cu^{2+} \rightarrow Cu$ 0.2 V

$Co^{2+} \rightarrow Co$ −0.3 V

$2H_2O \rightarrow H_2 + 2OH^-$ −0.4 V

$Mn^{2+} \rightarrow Mn$ −1.2 V

$Mg^{2+} \rightarrow Mg$ −2.4 V

What metals could be formed at [illegible] cathode in water? → reduction

$\boxed{Hg, Cu, Co}$

19.13 Corrosion

- product-favored oxidation of a metal exposed to environment (O_2, H^+, H_2O...

- requires both ~~cathode~~ anode half (metal) and cathode half:

$O_2 + 4H^+ \longrightarrow 2H_2O \quad E^\circ_{red} = 1.23$ V good!!

- metals with $E^\circ_{ox} > -1.23$ V are oxidized under acid conditions
  Most!! Exception: $\boxed{\text{gold!!}}$
- metals end as oxides or hydroxides
  Fe rusting
  Ag tarnish
  Cu "greening"

rust:

$2Fe + O_2 + 2H_2O \longrightarrow 2Fe(OH)_2$
↳ Fe_2O_3 red-brown rust

① corrosion often speeded by H^+, salt
② most metals get coated with film of hard oxide, protects interior
③ iron bad because rust flakes off, keeps exposing fresh metal

Prevention: ① coat surface
② "galvanize" - plate with Zn, which is more easily oxidized to give $Zn(OH)_2$ coating