Chapter 20

Electrochemistry

Electrochemical Cell

Consists of electrodes which dip into an electrolyte & in which a chem. rxn. uses or generates an electric current

Voltaic (Galvanic) Cell

Spont. rxn. - produces electrical energy

- current supplied to external circuit

Electrolytic Cell

electrical energy is used to drive an otherwise nonspont. rxn.

I) Oxidation - Reduction Rx's (Redox)

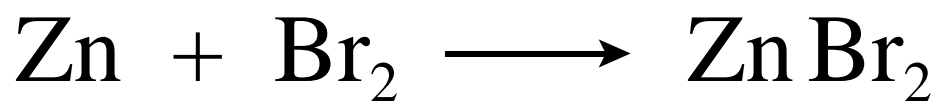Involves loss of e^- by one element & gain of e^- by another element

Oxidation: lose e^-

(inc. in oxidation #)

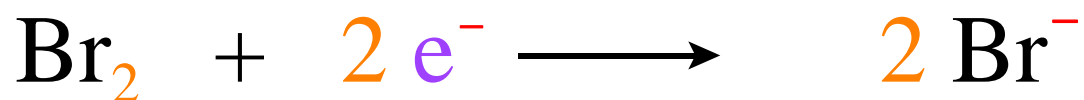Reduction: gain e^-

(dec. in oxidation #)

Oxidizing agent: substance that
(oxidant)   is reduced

Reducing agent: substance that
(reductant)   is oxidized

$$Zn + Br_2 \longrightarrow ZnBr_2$$

$$Zn \longrightarrow Zn^{2+} + 2\,e^-$$

Zn lost e^- $\Rightarrow$ oxidized

$$Br_2 + 2\,e^- \longrightarrow 2\,Br^-$$

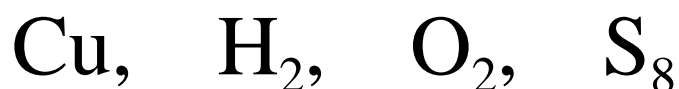Br gained e^- $\Rightarrow$ reduced

A) Oxidation Numbers

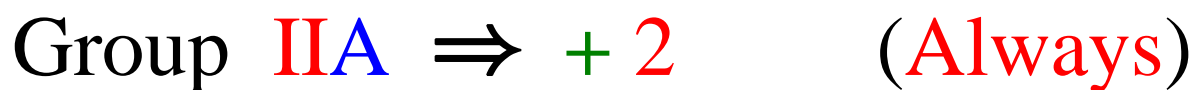"Charge" an atom would have if both e⁻ in each bond are assigned to the more electronegative atom.

1) Elemental Form

Cu, H$_2$, O$_2$, S$_8$

ox. # = 0 (zero)

2) Monatomic Ion

ox. # = charge

Na$^+$, Zn^{2+}, Al^{3+}, O^{2-}, Br$^-$

Group IA ⟹ + 1 (Always)

Group IIA ⟹ + 2 (Always)

Group IIIA ⟹ + 3 (usually)

3) Hydrogen

$H \Rightarrow +1$ (usually)

exceptions

hydrides, $H \Rightarrow -1$
NaH, CaH$_2$

4) Oxygen

$O \Rightarrow -2$ (usually)

exceptions

peroxides, O_2^{2-} $O \Rightarrow -1$
H$_2$O$_2$ Na$_2$O$_2$

superoxides, O_2^{1-} $O \Rightarrow -1/2$
KO$_2$
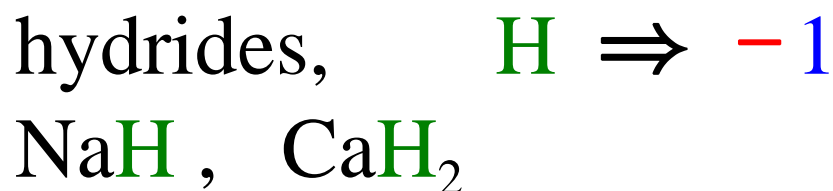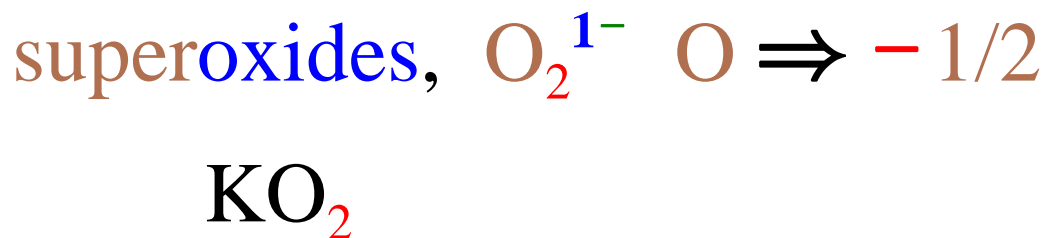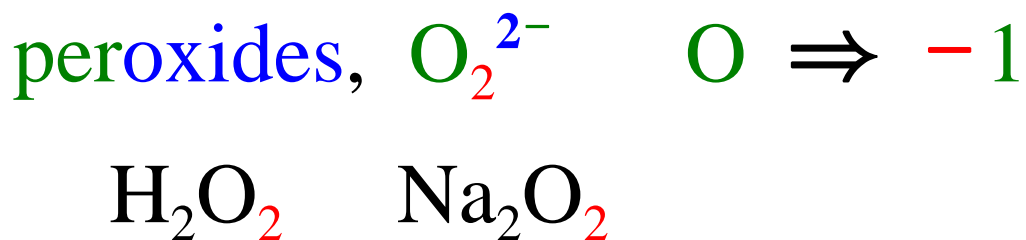
5) <u>Fluorine</u>

$F \Rightarrow -1$ Always

6) <u>Halogens</u>: Cl, Br, I

-1 except when combined
w. a more E.N. element

CBr_4 : $Br \Rightarrow -1$

can be : $-1, 0, +1, +3, +5, +7$

ClO_4^- : $+7$

7) Sum of ox. no.'s of atoms in neutral cmpds. =

0 (zero)

8) Sum of ox. no.'s of atoms in a polyatomic ion =

charge

9) Ox. no. can not be:

more positive than the group #

or

more negative than (group # − 8)

B) Examples

   1) Ex 1: What is ox. # of N in NH_3 ?

   $$x_N + 3(+1) = 0$$

   $$x_N = -3$$

   2) Ex 2: What is ox. # of N in NO_3^- ?

   $$x_N + 3(-2) = -1$$

   $$x_N = +5$$

   3) Ex 3: What is ox. # of N in NO_2^- ?

   $$x_N + 2(-2) = -1$$

   $$x_N = +3$$

4) <u>Ex 4</u>:   What is ox. # of Xe
in $XeOF_4$?

5) <u>Ex 5</u>:   What is ox. # of Cr
in $K_2Cr_2O_7$?

C) Redox Reactions

Involves transfer of e^- between species or change in ox. # of atoms

Oxidation: inc. in ox. #
                      (lose e^-)

Reduction: dec. in ox. #
                      (gain e^-)

1) Ex 1:   Combustion

$$CH_4 \; + \; 2\,O_2 \longrightarrow CO_2 \; + \; 2\,H_2O$$

2) <u>Ex 2</u>: What is being oxidized and reduced? What is the oxidizing agent and reducing agent? How many electrons are transferred?

$$P_4 \ + \ 10 \ HClO \ + \ H_2O \longrightarrow 4 \ H_3PO_4 \ + \ 10 \ HCl$$
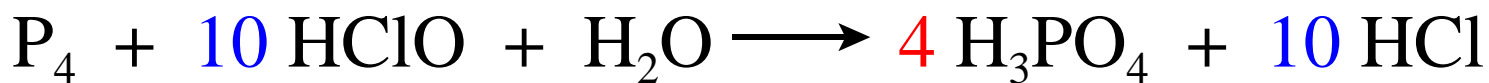
II) Balancing Redox Reactions

   A) Half-Reaction Method

focus on ox. & red. process separately

e⁻ lost in   # e⁻ gained in
ox. half-rx.   =   red. half-rx.

   1) Write eqn. in net ionic form

            Skeleton Eqn.

   2) Write 2 half-rx. - one for
         ox. & one for red.

   3) Determine coef. req. to balance
         atoms other than H & O

4) Bal. O atoms by adding H_2O
   to side needing O atoms

5) Bal. H atoms by adding H^+
   to side needing H atoms

   Acidic soln.

6) Bal. charge in each eqn. by
   adding e^- to more (+) side

red. ½-rx => e^- on reactant side
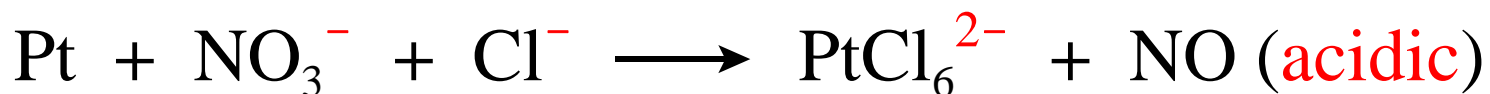
ox. ½-rx => e^- on product side

7) Multiply each ½-rx by factor so:

total # e^- lost = total # e^- gained

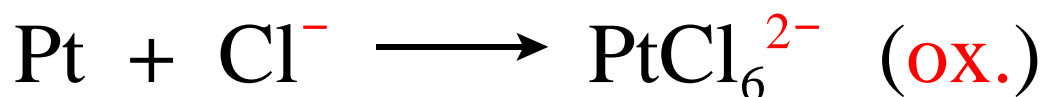7a) If rxn. in basic soln., add OH^- to both sides of ½-rxs. to neutralize H^+

Cancel H_2O as needed.

8) Add ½-rx & cancel e^- & other species common to both sides of eqn.

B) <u>Ex 1</u>: Bal. following redox eqn.
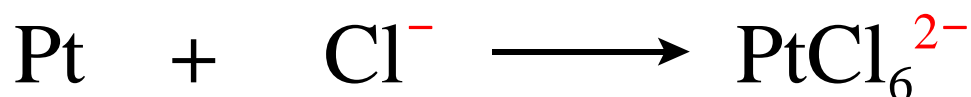in acidic soln.

$$Pt + NO_3^- + Cl^- \longrightarrow PtCl_6^{2-} + NO \text{ (acidic)}$$

1) <u>Step 2</u> - divide into ½-rx.

$$Pt + Cl^- \longrightarrow PtCl_6^{2-} \text{ (ox.)}$$

$$NO_3^- \longrightarrow NO \qquad \text{(red.)}$$

2) <u>Step 3</u> - bal. atoms other than O & H

$$Pt + Cl^- \longrightarrow PtCl_6^{2-}$$

3) <u>Steps 4 & 5</u> - Bal. O & H

$$NO_3^- \ + \qquad \longrightarrow \ NO \ +$$

4) <u>Step 6</u> - Bal. Charge

$$Pt \ + \ 6\,Cl^- \ \longrightarrow \ PtCl_6^{2-}$$

$$NO_3^- \ + \ 4\,H^+ \ \longrightarrow \ NO \ + \ 2\,H_2O$$
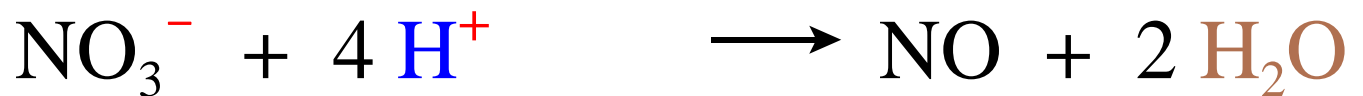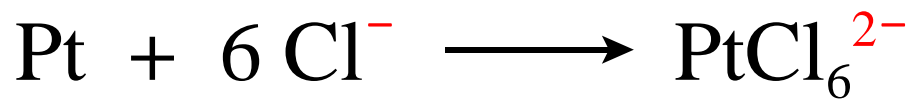
5) Step 7 - Multiply by factors so
e⁻ lost = # e⁻ gained

$$(Pt + 6\,Cl^- \longrightarrow PtCl_6^{2-} + 4\,e^-)$$

$$(NO_3^- + 4\,H^+ + 3\,e^- \longrightarrow NO + 2\,H_2O)$$

$$Pt + Cl^- \longrightarrow PtCl_6^{2-} + e^-$$

$$NO_3^- + H^+ + e^- \longrightarrow NO + H_2O$$
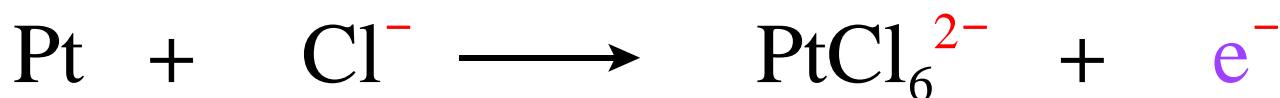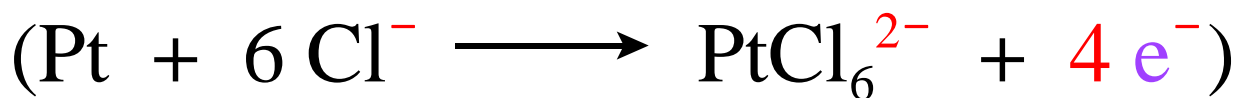
6) Step 8 - Add eqns & cancel

$$Pt + Cl^- + NO_3^- + H^+ \longrightarrow$$

$$PtCl_6^{2-} + NO + H_2O$$
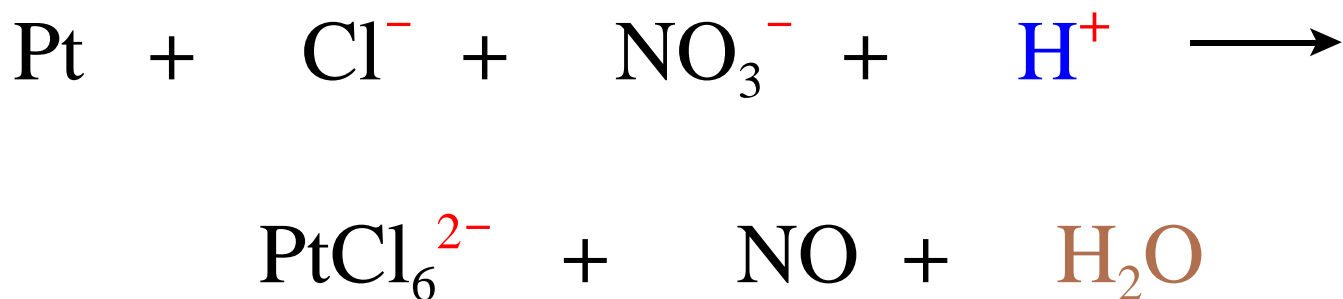
C) <u>Ex 2</u>: Bal. following redox eqn.
    in basic soln.

$MnO_4^- + Br^- \longrightarrow MnO_2 + Br_2$ (basic)

III) Voltaic (Galvanic) Cells

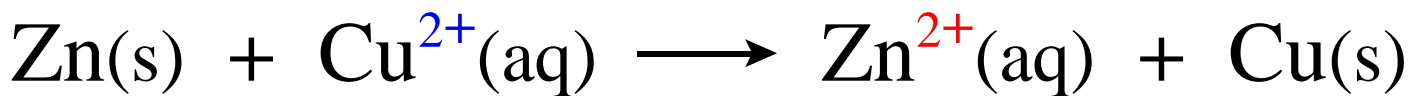Consists of 2 half-cells connected by an external circuit.

Half-cell

portion of an electrochem. cell in which a ½-rx occurs

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

Cell rxn :   net rxn. which occurs in the voltaic cell

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

Switch

1.10

Voltmeter

e^- e^-

Zn
anode NO_3^- Na^+

NO_3^- NO_3^- Cu
cathode
Zn^{2+} NO_3^-
NO_3^- Cu^{2+}

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

Movement of cations

Movement of anions

Electron flow

Anode   −   Porous barrier   +   Cathode
or salt bridge

Anions

Cations

Anode compartment   Cathode compartment
Oxidation occurs   Reduction occurs

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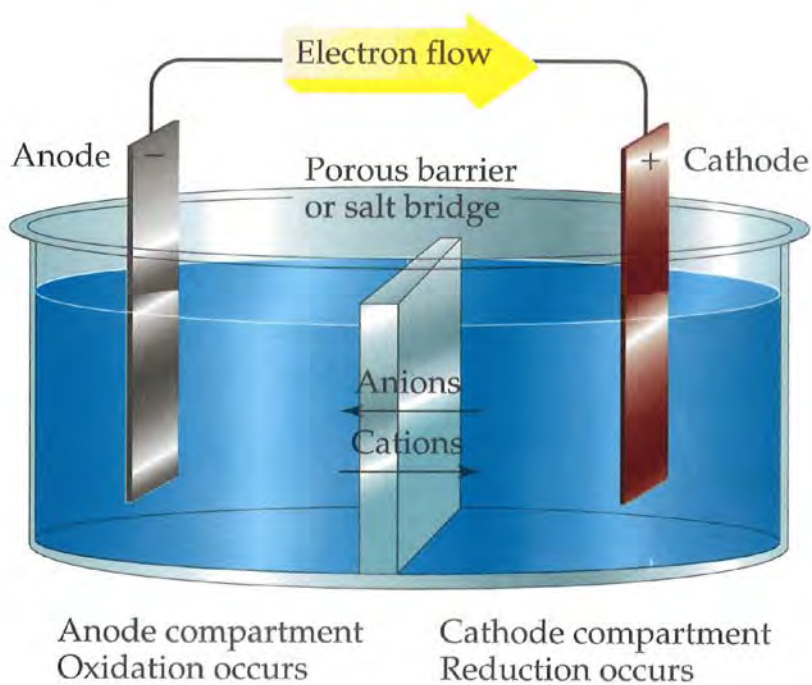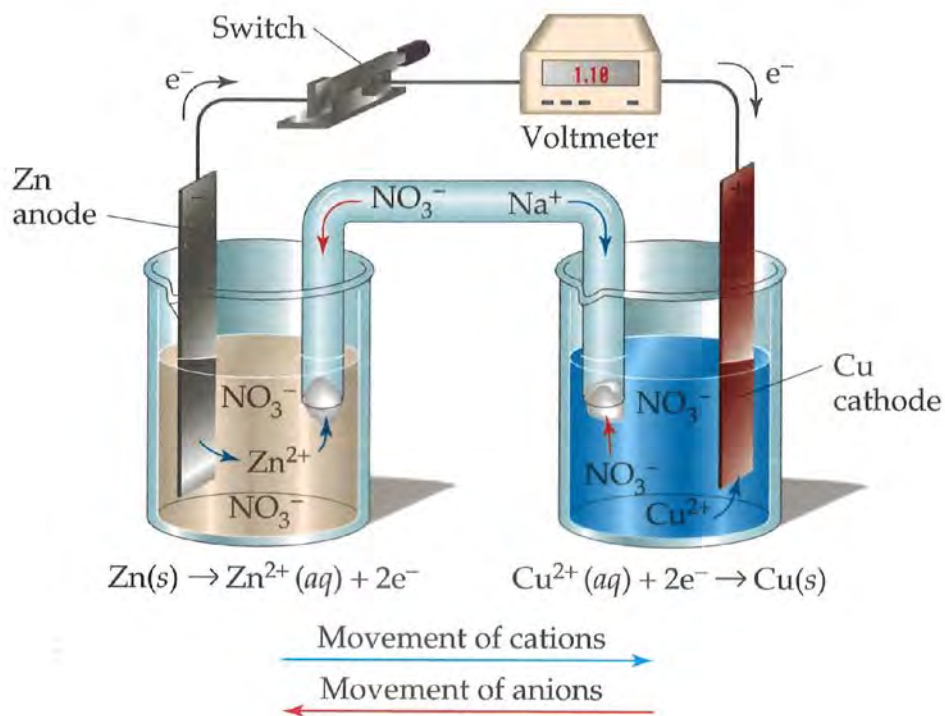
A) Half-cell Rxns

1) Anode (–)

Anode :   electrode at which

ox. occurs

ox. half-rx

$$Zn\,(s) \longrightarrow Zn^{2+}\,(aq) \; + \; 2\,e^-$$

Zn^{2+} ions produced at electrode

- move away leaving e^- behind

e^- flow out of anode

(towards the cathode)

2) <u>Cathode</u>   (+)

Cathode : electrode at which
red. occurs

red. half-rx

$$Cu^{2+} \text{ (aq)} \quad + \quad 2\, e^- \longrightarrow Cu \text{ (s)}$$

Cu^{2+} ions discharged at electrode

- removes e^- from electrode

e^- flow into the cathode

(appears to attract e^-)

Soln. on right has a − chg.

Soln. on left has a + chg.

anions must move from

lt. ⟵ rt.

Accomplishes 2 things

1) Carry chg.

2) Preserves electrical neutrality

Salt Bridge

tube of electrolyte in a gel connected to the half-cells

- allows flow of ions but prevents mixing of the diff. solns.

B) Cell Notation

Shorthand description of cell

1) Ions in soln.

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

anode   salt   cathode
bridge

$\mid$ vertical line is a phase boundary

begin & end w. electrodes

anode :

cathode :

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2) Gaseous Reactant or Product

use inert electrode

$$Zn(s) \mid Zn^{2+}(aq) \parallel Cl_2(g) \mid Cl^-(aq) \mid Pt$$

anode   salt   cathode
bridge

anode :

cathode :

3) Ions in Diff. Ox. States

use inert electrode

$$Sn(s) \mid Sn^{2+}(aq) \parallel Sn^{4+}(aq), Sn^{2+}(aq) \mid Pt$$

anode   salt   cathode

bridge
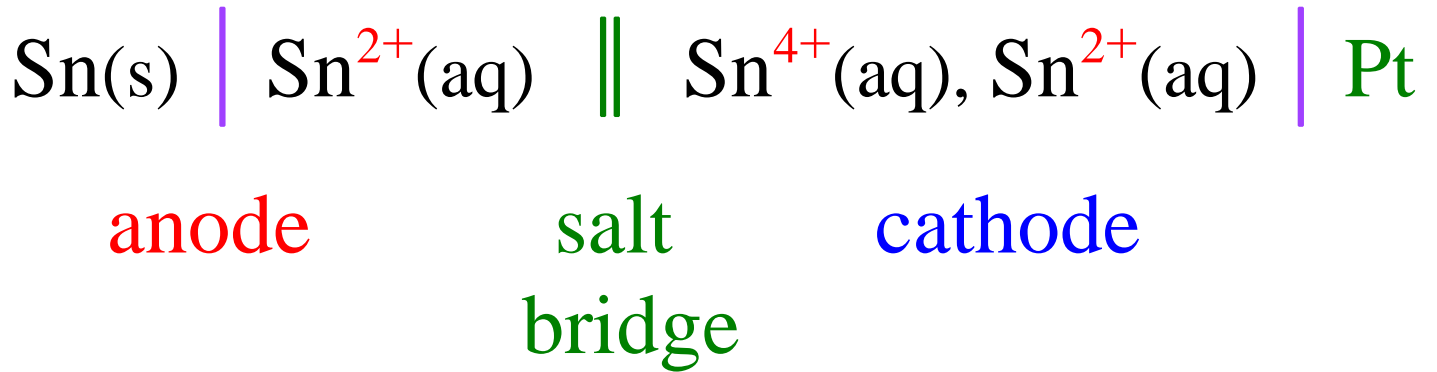
anode :

cathode :

IV) Standard Cell (Electrode) Potentials

A) Electromotive Force

Work req. to move a charge from
a region of low electric pot. energy
to a region of high electric pot. energy.

$$w = \text{charge} \times \Delta\text{P.E.}$$

Joules = Coulombs • Volts

$$1\ J = 1\ C \cdot V$$

ΔP.E. (V) : diff. in electric potential
between 2 points

work done by a voltaic cell to move n moles of e^- is given by:

$$w_{max} = - n F E_{cell}$$

F : faraday constant, 9.65×10^4 C

charge on 1 mole of e^-

E_{cell} : electromotive force (emf)

max. potential diff. between electrodes of a cell
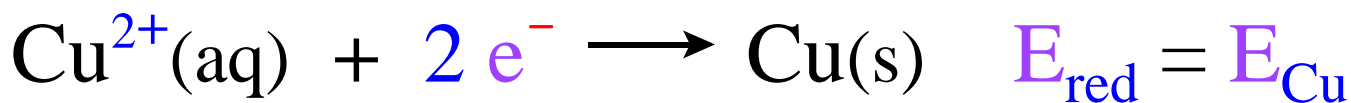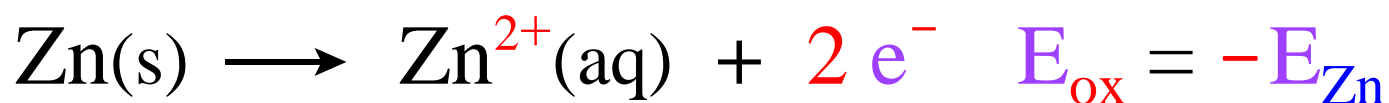
$$\Delta G = - n F E_{cell}$$

NOTE :   Spont. rxn.

$$\Delta G < 0 \qquad E_{cell} > 0$$

B) Cell (Electrode) Potentials

$$E_{cell} = E_{red} + E_{ox}$$

$$E_{ox} = -E_{red} \text{ for reverse rxn.}$$

Tabulate reduction pot.
called electrode pot., E_{red}

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^- \quad E_{ox} = -E_{Zn}$$

$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s) \quad E_{red} = E_{Cu}$$

$$E_{cell} = E_{Cu} + (-E_{Zn})$$

$$= E_{Cu} - E_{Zn}$$

$$\boxed{E_{cell} = E_{cathode} - E_{anode}}$$

C) Standard Reduction Potentials

Standard emf : E^o_{cell}

emf of a cell under standard-state conditions

Standard reduction pot. E^o_{red}

reduction (electrode) pot. when conc. of solutes are 1 M & gas pressures are 1 atm, at a specified temp.

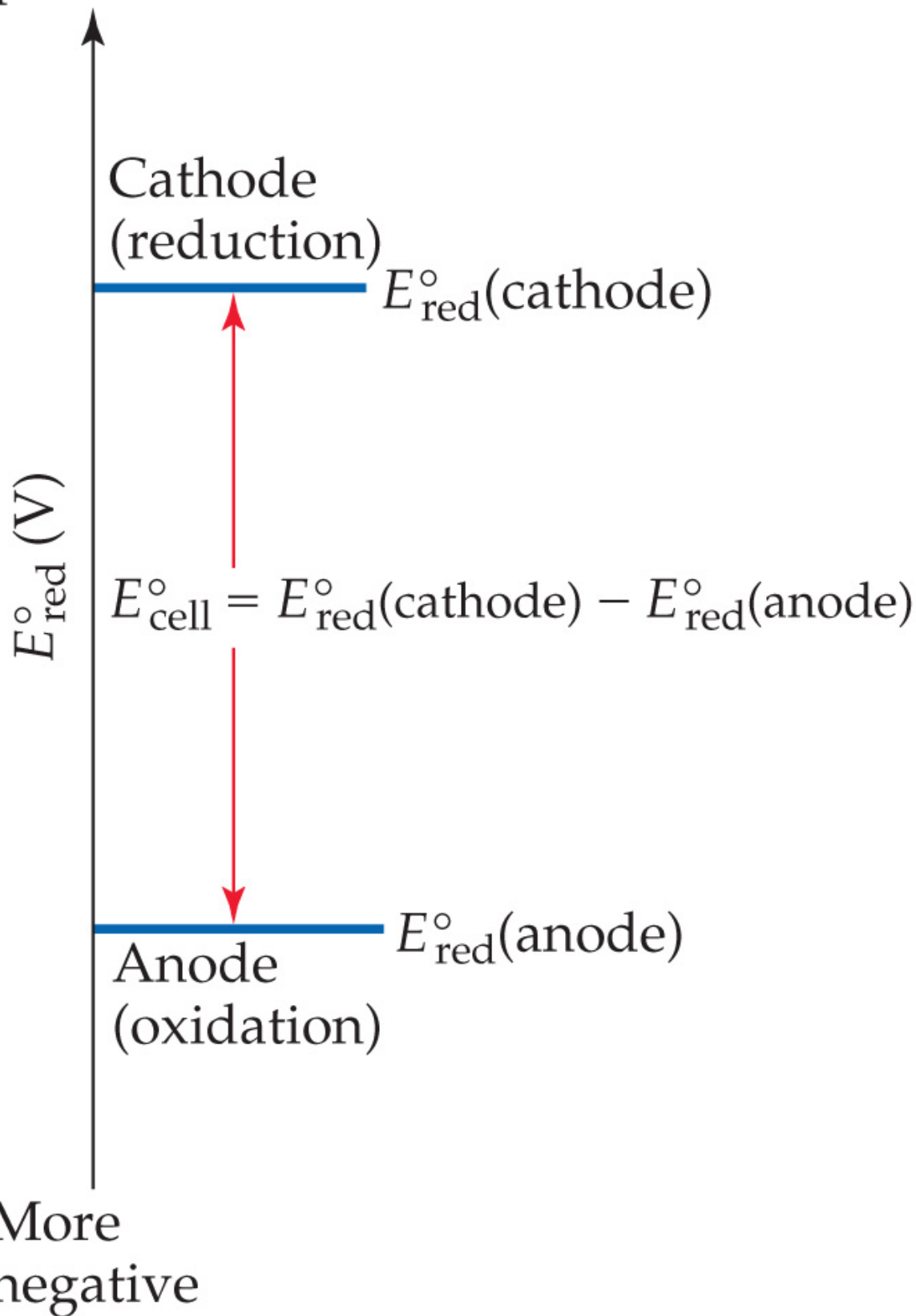- measured relative to a reference electrode
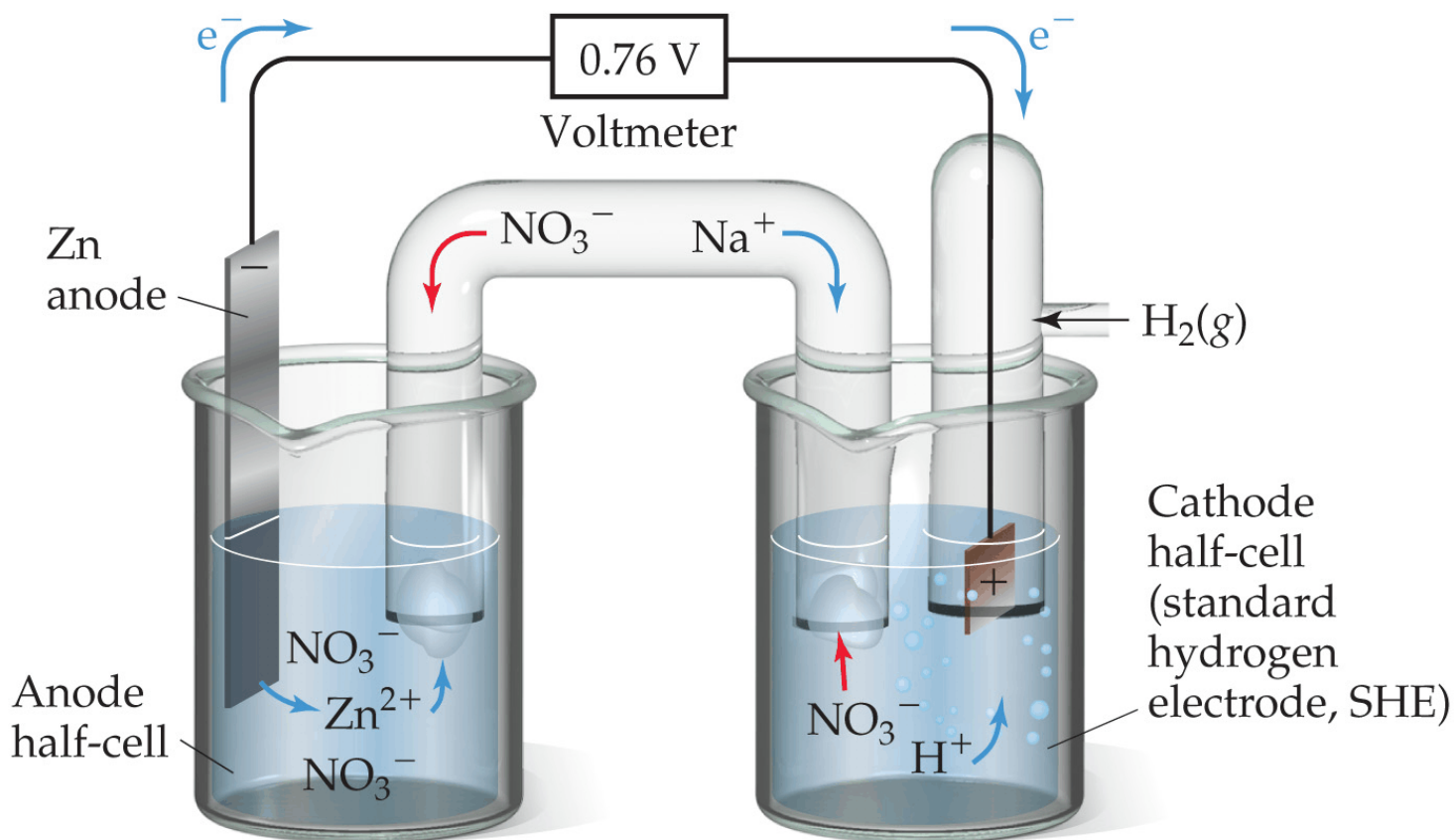
- standard H electrode (SHE)

$$2\,H^+ \,(aq) \; + \; 2\,e^- \longrightarrow H_2 \,(g)$$

$$E^o_{H_2} = 0.00\ V$$

More
positive

E_{red}° (V)

Cathode
(reduction) ___ E_{red}°(cathode)

$E_{cell}^{\circ} = E_{red}^{\circ}$(cathode) $- E_{red}^{\circ}$(anode)

___ E_{red}°(anode)

Anode
(oxidation)

More
negative

TABLE 20.1 • Standard Reduction Potentials in Water at 25 °C

E°_{red} (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$
+1.51	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$
+1.36	$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$
+1.23	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$
+1.06	$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$
+0.96	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$
+0.54	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$
+0.40	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$
0 [defined]	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$
−0.83	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Zn anode

0.76 V
Voltmeter

NO_3^- Na^+

$H_2(g)$

Zn anode

Anode half-cell

NO_3^-
Zn^{2+}
NO_3^-

NO_3^-
H^+

Cathode half-cell (standard hydrogen electrode, SHE)

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$ $2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$

D) Strengths of Ox. & Red. Agents

Arranged in table w. greatest tendency for red. at top

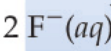Strongest ox. agents are at the upper left (F_2, $S_2O_8^{2-}$, H_2O_2)

Strongest red. agents are at the lower right (Li, Na, Mg, Al)

Note

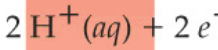For a spont. rxn the stronger ox. & red. agents will be the reactants

Most positive values of $E°_{red}$
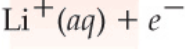
Easiest to reduce, strongest oxidizing agent

$F_2(g) + 2\,e^-$ → $2\,F^-(aq)$

Most difficult to oxidize, weakest reducing agent

Increasing strength of oxidizing agent

Increasing strength of reducing agent

$2\,H^+(aq) + 2\,e^-$ → $H_2(g)$

Most difficult to reduce, weakest oxidizing agent

$Li^+(aq) + e^-$ → $Li(s)$

Easiest to oxidize, strongest reducing agent

Most negative values of $E°_{red}$

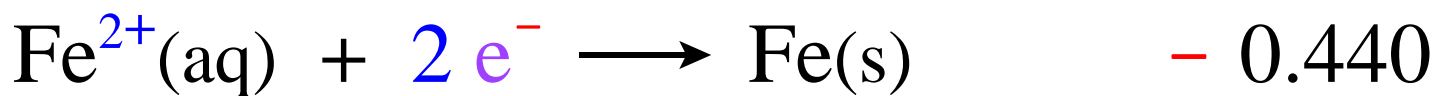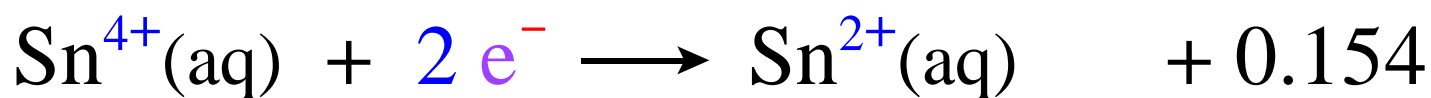© 2012 Pearson Education, Inc.

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TABLE 20.1 • Standard Reduction Potentials in Water at 25 °C

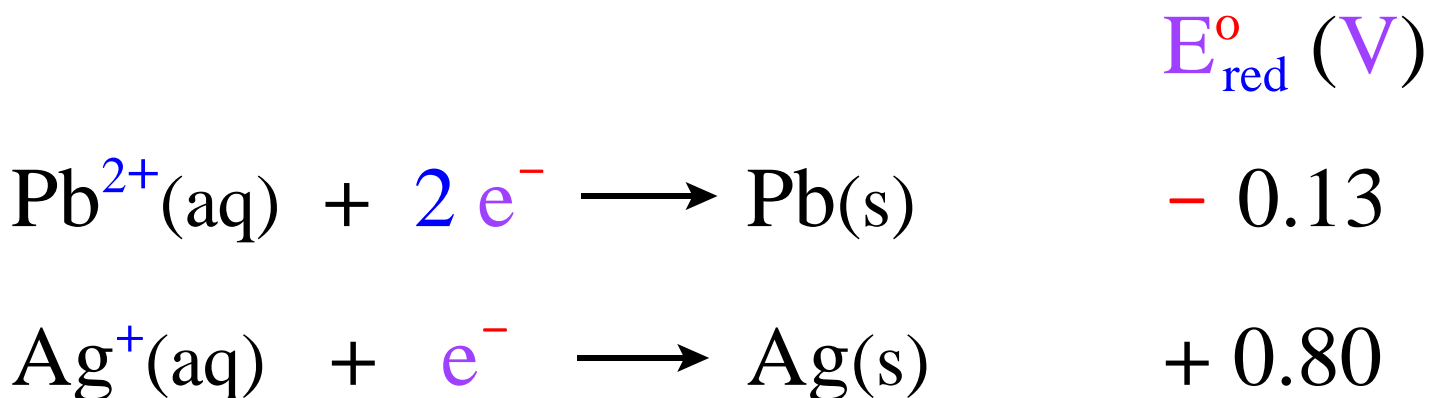| E°_{red} (V)	Reduction Half-Reaction
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−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

1) <u>Ex 1</u> : Which will be the stronger red. agent under standard conditions, Sn^{2+} (to Sn^{4+}) or Fe (to Fe^{2+})

$$E^o_{red} \text{ (V)}$$

$$Sn^{4+}(aq) + 2\ e^- \longrightarrow Sn^{2+}(aq) \qquad + 0.154$$

$$Fe^{2+}(aq) + 2\ e^- \longrightarrow Fe(s) \qquad - 0.440$$

E) Calc. Cell emf's from Std. Pot.

$$E^o_{red} \ (V)$$

$$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s) \qquad -\,0.13$$

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad +\,0.80$$

1) rxn. is spont. w. stronger red. agent (one most easily ox.) on left (as reactant), Pb
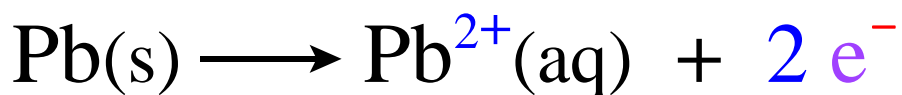
Reverse of Pb electrode rxn.

NOTE: For a voltaic cell the cathode must be rxn. w. more + E^o_{red}

- Ag electrode in this case

$$Pb(s) \longrightarrow Pb^{2+}(aq) + 2\,e^-$$

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$
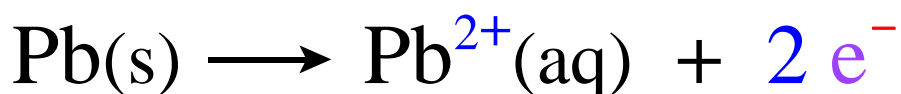
2) Multiply rxn. 2 (Ag rxn) by 2
to balance the e^-

E^o_{red} NOT multiplied by factor

- intensive quantity

$$Pb(s) \longrightarrow Pb^{2+}(aq) + 2\,e^-$$

$$2\,Ag^+(aq) + 2\,e^- \longrightarrow 2\,Ag(s)$$

3) Add eqns to get overall cell rxn

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

$$Pb(s) \mid Pb^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$$
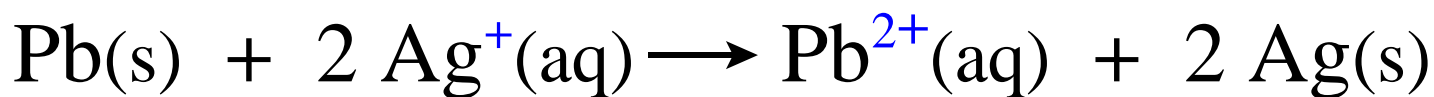
4) Calc. cell potential, E^o_{cell}

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$= E^o_{Ag} - E^o_{Pb}$$

II) Equilibrium Constants from emf's

$$\Delta G^\circ = -n F E^\circ_{cell}$$

Also,

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

$$\therefore \quad n F E^\circ_{cell} = RT \ln K$$

$$E^\circ_{cell} = \frac{RT}{nF} \ln K$$

or

$$E^\circ_{cell} = \frac{2.303 \, R \, T}{n \, F} \log K$$

At 25°C

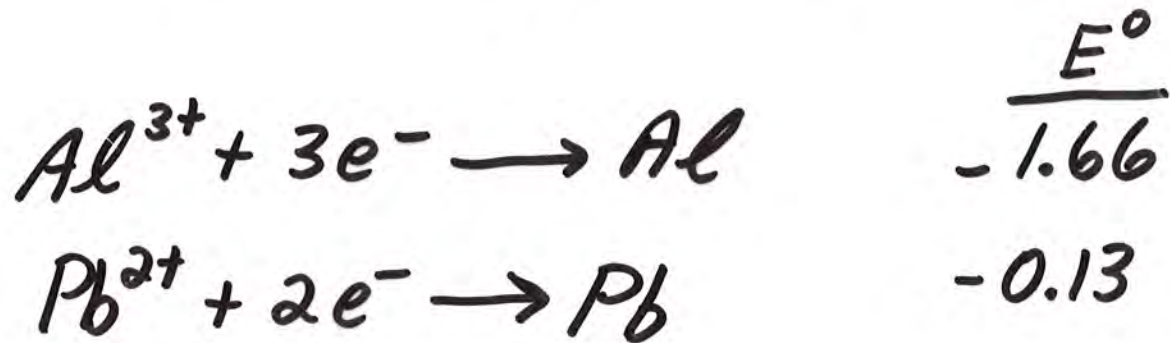$$E^\circ_{cell} = \frac{0.0592}{n} \log K \quad \text{(in volts)}$$

A) Ex's

1) Calc. ΔG° at 25°C For the Pb-Ag cell.

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

2) Calc. the equil. constant K.

$$E^\circ_{cell} = \frac{0.0592}{n} \log K$$

B) <u>Ex 2</u> : what are ΔG° and K for the following cell?

$$Al(s)\,|\,Al^{3+}(aq)\,||\,Pb^{2+}(aq)\,|\,Pb(s)$$

$$
\begin{array}{ll}
 & \underline{E^{\circ}} \\
Al^{3+} + 3e^- \longrightarrow Al & -1.66 \\
Pb^{2+} + 2e^- \longrightarrow Pb & -0.13
\end{array}
$$

VI) Dependence of emf on Conc.

A) Nernst Equation

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

$$-nFE_{cell} = -nFE^{\circ}_{cell} + RT \ln Q$$

$$\boxed{E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln Q}$$

At $25^{\circ}C$,

$$\boxed{E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q}$$

(in volts)

1) **Ex** : Determine the voltage of the following cell:

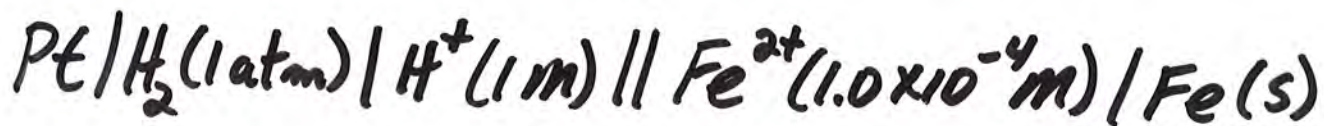$$Cr \mid Cr^{3+} (0.010m) \parallel Pb^{2+} (1.00m) \mid Pb$$

B) Electrode Pot. for Non Standard Conditions

Can use the Nernst eqn to find the **electrode pot.** when **conc.** is **not 1 M** &/or pressure is **not 1 atm**

1) **Ex**: what is the pot. of the iron electrode $Fe^{2+}(aq)|Fe(s)$ when the Fe^{2+} conc. is $1.0 \times 10^{-4} m$?

$Pt|H_2(1\,atm)|H^+(1m)\|Fe^{2+}(1.0 \times 10^{-4}m)|Fe(s)$

$$E_{cell} = E(Fe^{2+}/Fe) - E^o(H^+/H_2)$$

$$= E(Fe^{2+}/Fe)$$

Using Nernst eqn.,

$$E(Fe^{2+}|Fe) = E^\circ(Fe^{2+}|Fe) - \frac{0.0592}{n} \log Q$$

To find n & exp. for Q write overall rx.

$$Fe^{2+}(aq) + H_2(g) \rightleftharpoons Fe(s) + 2H^+(aq)$$

$$n = 2 \qquad \&$$

$$Q = \frac{[H^+]^2}{[Fe^{2+}] P_{H_2}} = \frac{1^2}{[Fe^{2+}] \cdot 1} = \frac{1}{[Fe^{2+}]}$$

$$\therefore \quad E(Fe^{2+}|Fe) = E^\circ(Fe^{2+}|Fe) - \frac{0.0592}{2} \log \frac{1}{[Fe^{2+}]}$$

$$= -0.41 - 0.1184$$

$$= -0.53 \text{ V}$$

2) *Ex* : Determine unknown conc. of Cd^{2+}.

$$Cd \mid Cd^{2+}(aq, ?M) \parallel Ag^{+}(1m) \mid Ag$$

$$Cd + 2Ag^{+} \longrightarrow Cd^{2+} + 2Ag$$

measure $E_{cell} = 1.44 V$

$$E_{cell} = E^{0}_{cell} - \frac{0.0592}{n} \log \frac{[Cd^{2+}]}{[Ag^{+}]^{2}}$$

$$1.44 = 1.20 - \frac{0.0592}{2} \log [Cd^{2+}]$$

$$\log [Cd^{2+}] = -8.11$$

$$[Cd^{2+}] = 7.8 \times 10^{-9} M$$

C) Determination of pH

$$Pt \mid H_2(1\,atm) \mid H^+(test\,soln) \parallel H^+(1m) \mid H_2(1\,atm) \mid Pt$$

E_{cell} is due to *test* soln. half-cell

$$\tfrac{1}{2} H_2(1\,atm) \rightleftharpoons H^+(test\,soln.) + e^-$$

$$E_{cell} = -0.0592 \log[H^+] , 25°C$$
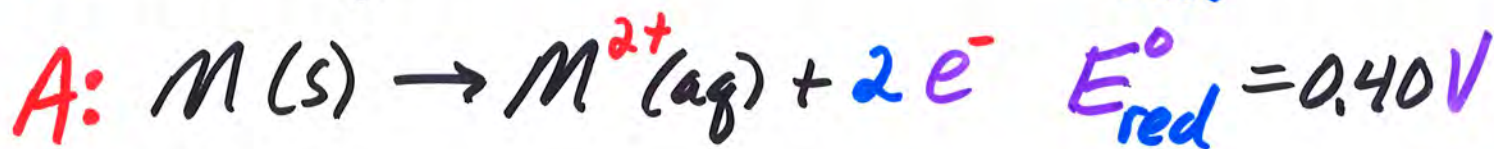
or

$$pH = \frac{E_{cell}}{0.0592}$$

D) Concentration Cells

Cell based solely on emf generated bec. of diff. in conc.

Use same electrode for both cathode & anode

- diff. conc. in each ½-cell

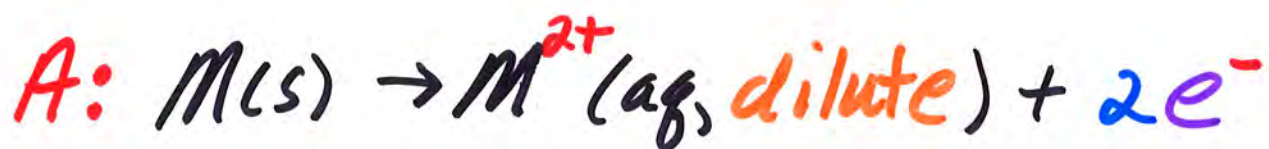E^0_{red} is same for both electrodes

C: $M^{2+}(aq) + 2e^- \rightarrow M(s)$ $E^0_{red} = 0.40V$

A: $M(s) \rightarrow M^{2+}(aq) + 2e^-$ $E^0_{red} = 0.40V$

$$E^0_{cell} = E^0_{cat} - E^0_{an}$$

$$= (0.40\ V) - (0.40\ V)$$

$$= 0\ V$$

For a *voltaic cell* ox. occurs in $\frac{1}{2}$-cell containing the **more** *dilute* soln.

— *anode*

A: $M(s) \rightarrow M^{2+}(aq, dilute) + 2e^-$

C: $M^{2+}(aq, conc) + 2e^- \rightarrow M(s)$

$$\overline{M^{2+}(aq, conc) \rightarrow M^{2+}(aq, dilute)}$$

$$E_{cell} = E^0_{cell} - \frac{0.0592V}{n} \log Q$$

$$= 0 - \frac{0.0592V}{n} \log \frac{[M^{2+}]_{dilute}}{[M^{2+}]_{conc}}$$

$$E_{cell} = - \frac{0.0592V}{n} \log \frac{[M^{2+}]_{dilute}}{[M^{2+}]_{conc}}$$

Note:

For voltaic cell Q is

$$\frac{[dilute]}{[conc]}$$

1) Ex: What is the E_{cell} using a Cu electrode w. Cu^{2+} conc. of 0.00100 M and 2.00 M?

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E^0 = +0.337 \text{ V}$$

VII) Practical Applications

A) Corrosion Protection

Iron rusts

$$Fe \longrightarrow Fe^{2+} + 2e^- \qquad OX.$$

Place Fe in contact w.
a more active metal
(more easily oxidized)

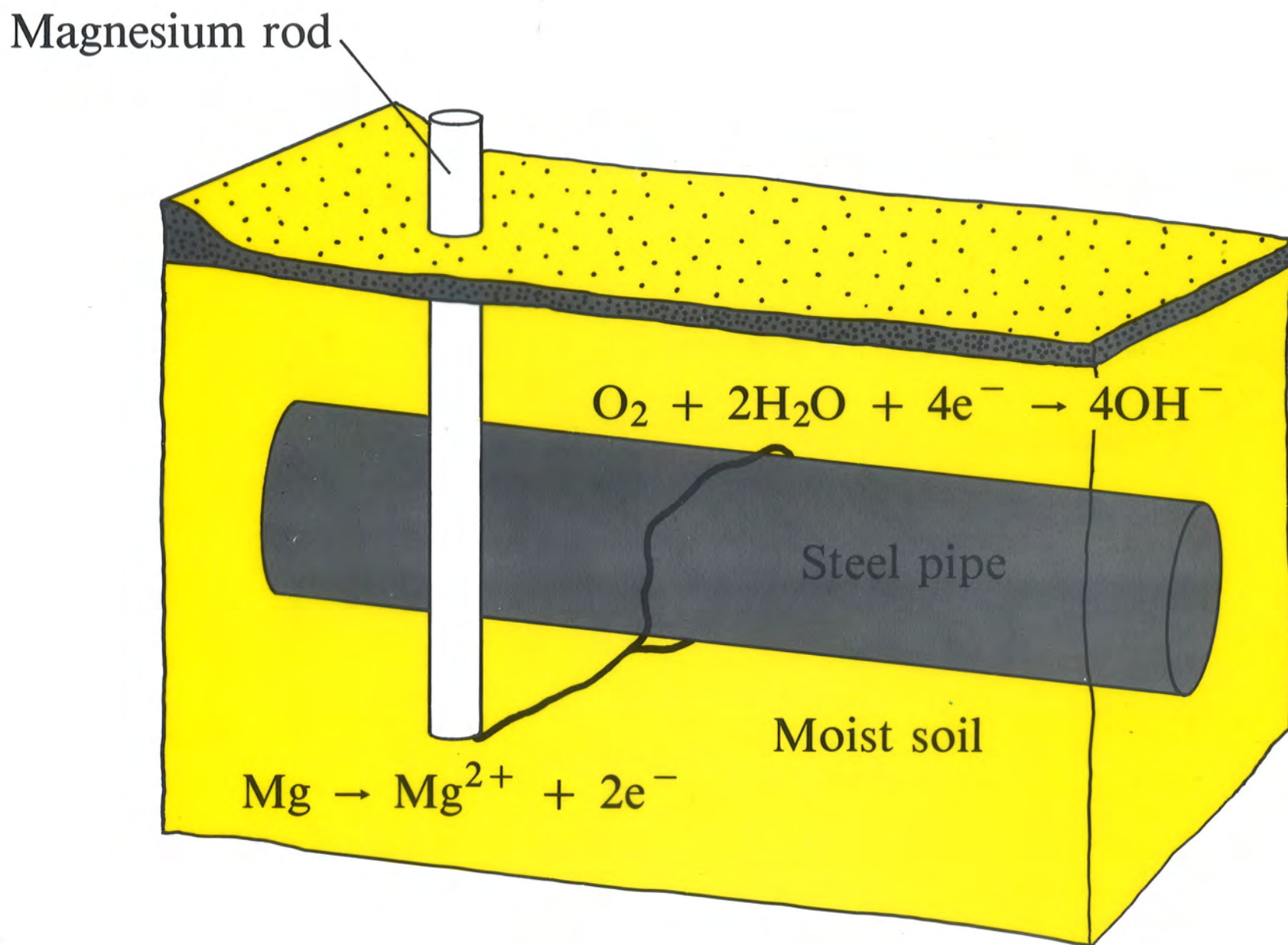Fe/Fe^{2+} becomes cathode

Metal becomes anode

Cathodic Protection

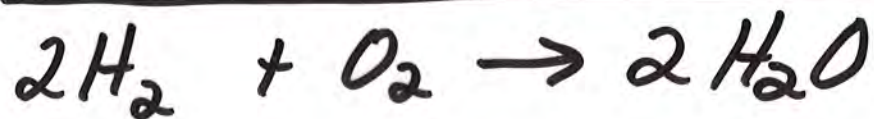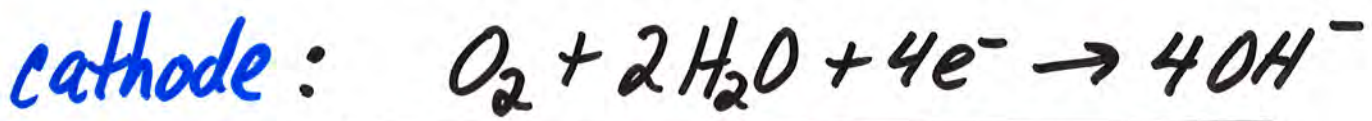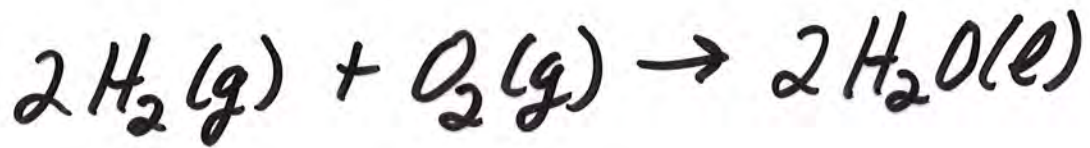1) <u>*Underground Pipe*</u>

Fe pipe connected to
Mg or Zn rod

$$Mg + Fe^{2+} \rightarrow Mg^{2+} + Fe$$

2) <u>*Galvanized Iron*</u>

coat w. Zn

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

Magnesium rod

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

Steel pipe

Moist soil

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

B) *Fuel Cells*

Convert energy of combustion directly into electrical energy

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

$$C \mid H_2(g) \mid OH^-(aq) \mid O_2(g) \mid C$$

anode : $(H_2 + 2OH^- \rightarrow 2H_2O + 2e^-)2$

cathode : $\dfrac{O_2 + 2H_2O + 4e^- \rightarrow 4OH^-}{2H_2 + O_2 \rightarrow 2H_2O}$

60-70 % efficient

Calorimetric data
ΔH°, ΔS°

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Composition data

ΔG°

$\Delta G^\circ = -nFE^\circ_{cell}$

Electrochemical data
E°_{cell}

$E^\circ_{cell} = \dfrac{RT}{nF} \ln K$

Equilibrium constants
K
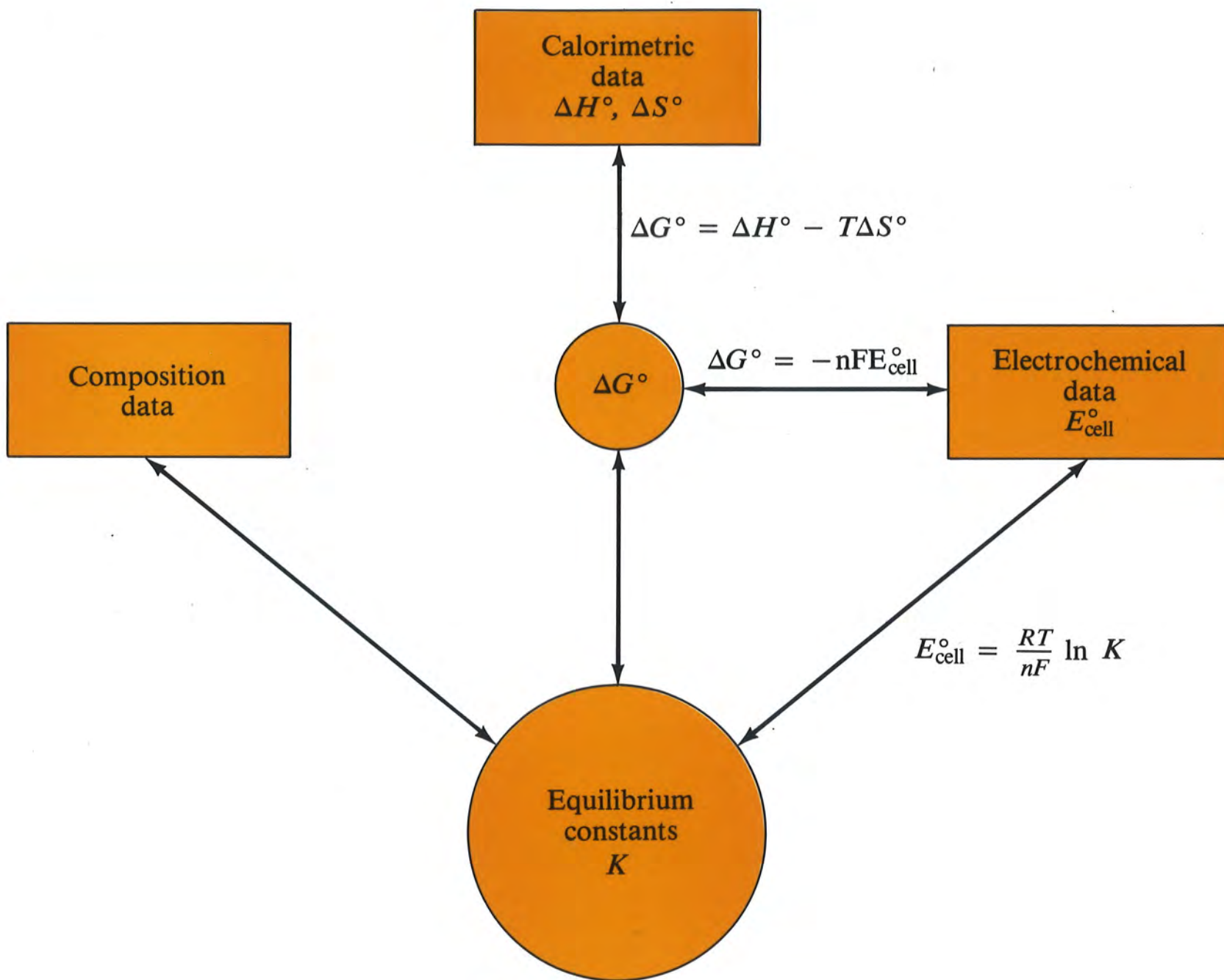
IX) Electrolytic Cells

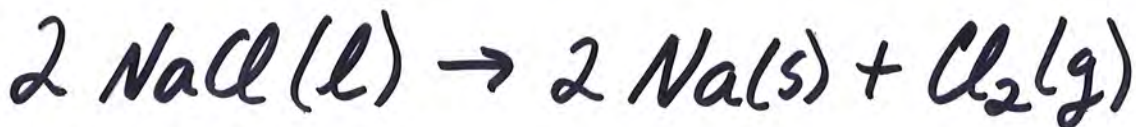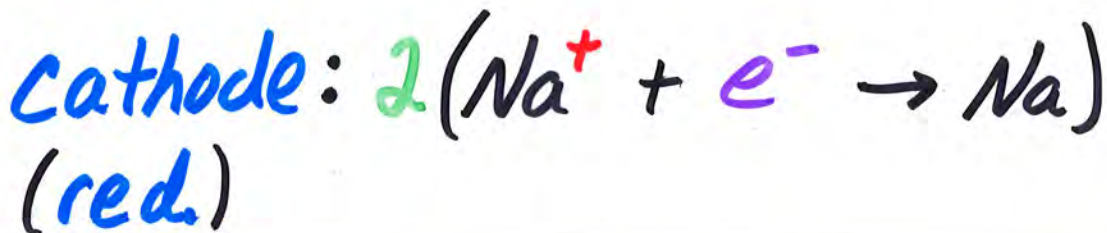Energy from *external* source is *used* to bring about a *non* *spont.* chem. rx.
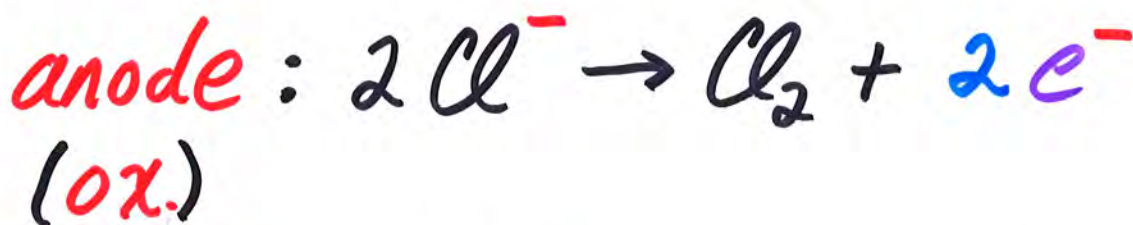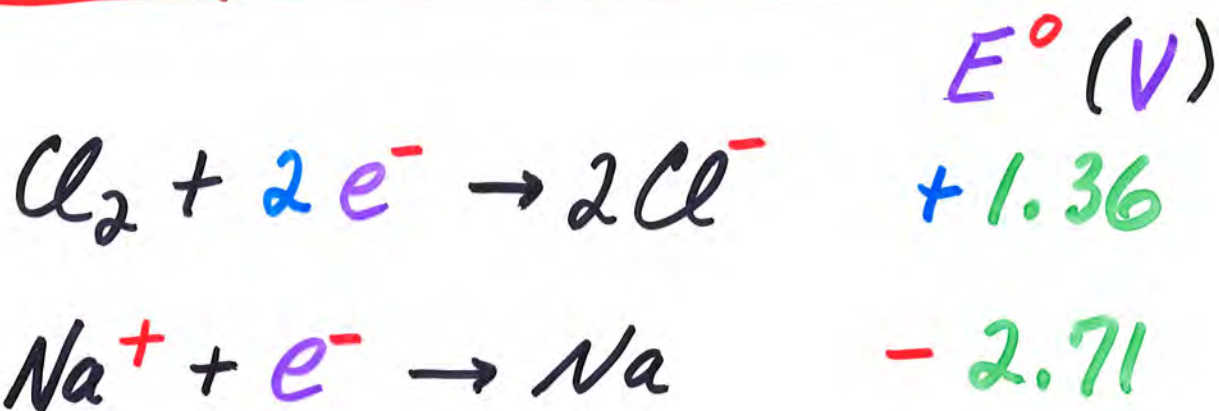
Cell is *driven* by a *battery*

- Acts as an e^- pump
  - pushes e^- *onto* one electrode & *pulls* them from another
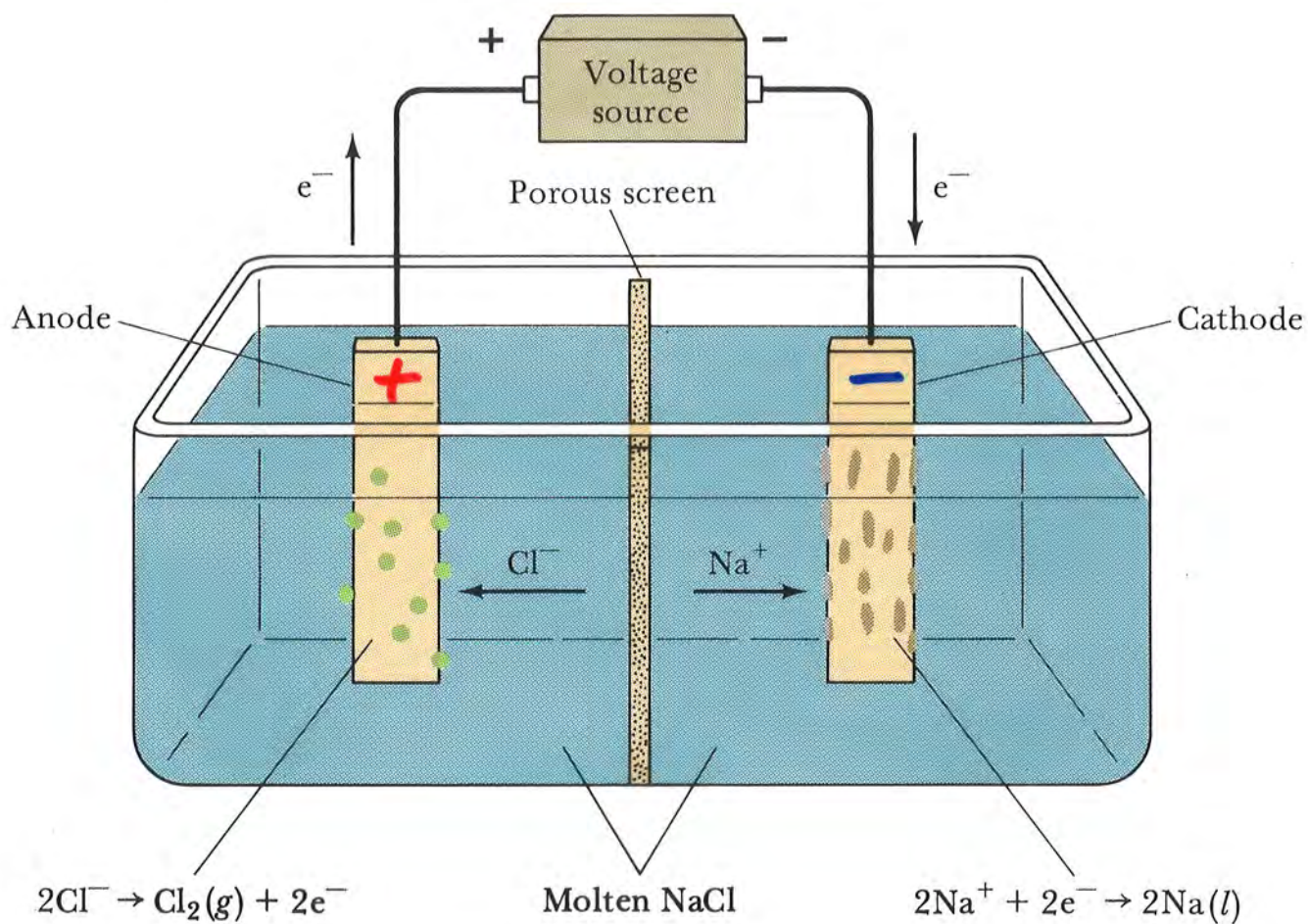
A) Electrolysis of Molten NaCl

$$E^\circ \ (V)$$

$$Cl_2 + 2e^- \rightarrow 2Cl^- \qquad +1.36$$

$$Na^+ + e^- \rightarrow Na \qquad -2.71$$

anode : $2Cl^- \rightarrow Cl_2 + 2e^-$
(ox.)

cathode: $2(Na^+ + e^- \rightarrow Na)$
(red.)

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

29

1) E°_{cell}

$$E^{\circ}_{cell} = E^{\circ}_{cat} - E^{\circ}_{an}$$

$$= E^{\circ}_{Na} - E^{\circ}_{Cl_2}$$

$$= (-2.71) - (+1.36)$$

$$= -4.07 \text{ V}$$

Non spont.

Note: sign convention for electrodes is opposite that for voltaic cells

Figure 20.16 Electrolysis of molten sodium chloride

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

Molten NaCl

$2Na^+ + 2e^- \rightarrow 2Na(l)$

X) *Stoichiometry of Electrolysis*

How much product is formed?
How long will it take?

$$1 \, C = 1 \, A \cdot s$$

$$1 \, F = 96{,}500 \, C/\text{mole } e^-$$

A current of 0.50 A flowing
for 84 seconds gives a charge of,

$$0.50 \, A \times 84 \, s = 42 \, C$$

A) *Time* and *Amount*

1)Ex: Chrome-plate an object.
How long would it take to
deposit 35.5g Cr from a
soln. of $CrCl_3$ at a current
of 6.00 A ?

$$Cr^{3+} + 3e^- \rightarrow Cr \quad (cathode)$$
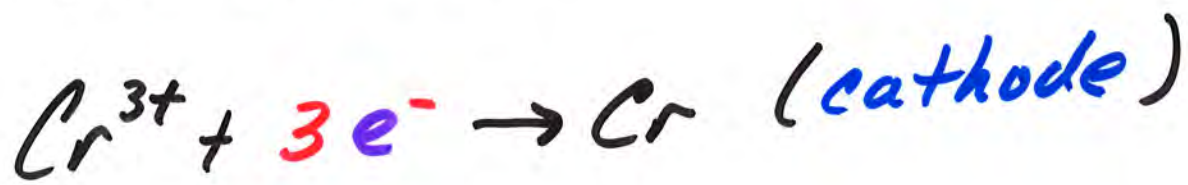
3 mole e^- req. for each mole Cr

a) How fast does this occur?
$$6.00 A = 6.00 \; C/s$$

b) How many grams of Cl_2 are produced?

B) Electrical Work

1) Voltaic Cell

$$w_{max} = -nFE_{cell}$$

$$-w_{max} \quad (w_{max} < 0)$$

$$\Rightarrow \text{spont.}$$

(max work obtainable)

2) Electrolytic Cell

Non spont. $(\Delta G > 0, E < 0)$

— supply external potential

$$w = nFE_{ext}$$

surr. doing work on system

3) Units

Electrical work usually expressed in energy units of

watts x time

$$1 \text{ W} = 1 \text{ J/s}$$

electric utilities use kW-hour

$$1 \text{ kWh} = (1000 \text{ W})(1 \text{ hr})\left(\frac{3600 \text{ s}}{1 \text{ hr}}\right)\left(\frac{1 \text{ J/s}}{1 \text{ W}}\right)$$

$$= 3.6 \times 10^{6} \text{ J}$$

4) **Ex**: What applied **emf** is required to produce $2.0 \times 10^3 kg$ of Al by electrolysis of Al^{3+} if $1.0 \times 10^4 kWh$ of electricity is used?