

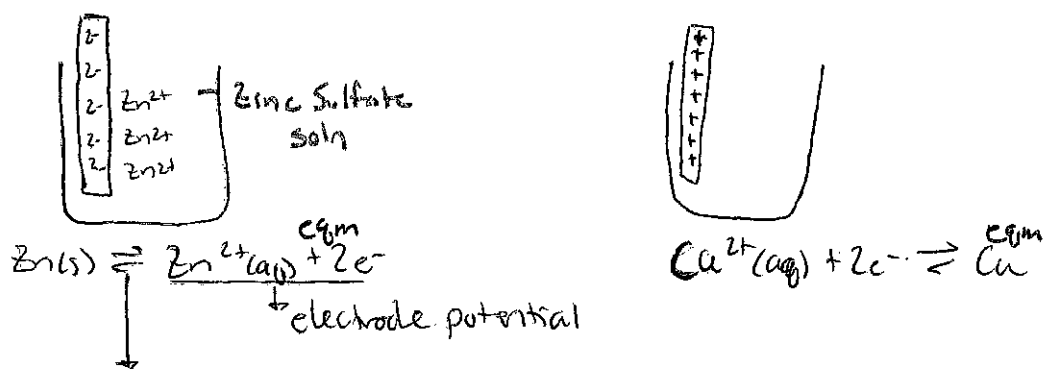
9.2 + 19.1 Electrochemical Cells

Voltaic Cells

Spontaneous redox rxns can be organized to generate an electric current

Separate 2 $\frac{1}{2}$ rxns into half-cells \rightarrow allowing e^- to flow through external circuit
(electrochemical / galvanic / voltaic cell)

\downarrow
generate electrode potentials



position of eqm determines size of potential in $\frac{1}{2}$ cell & depends on reactivity

Two connected $\frac{1}{2}$ cells make a voltaic cell

• connect w/ external wire $\rightarrow e^-$ flows from (-) to (+)
(Zn \rightarrow Cu)

electrodes: anode: ox occurs
 $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

cathode: red occurs
 $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

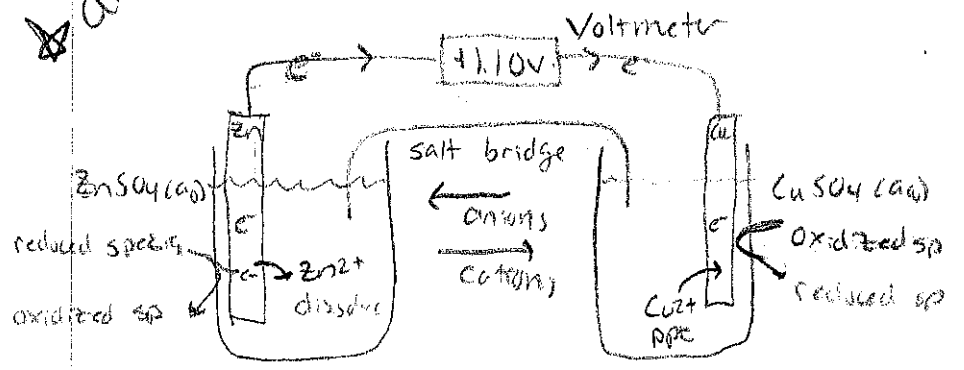
} no longer eqm when circuit is complete

Voltaic cell w/ proper connections:

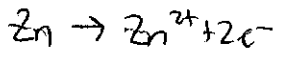
- electrical wire: connected to each metal + Voltmeter
- salt bridge: completes circuit

glass tube / absorptive paper - contains aq soln of ion (NaNO₃ / KNO₃) → enables (-) to be carried in opposite direction → neutralizes any charge build up to maintain potential difference

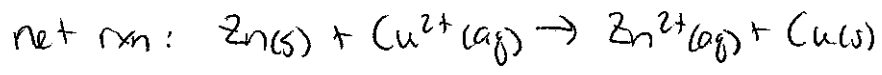
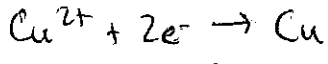
draw



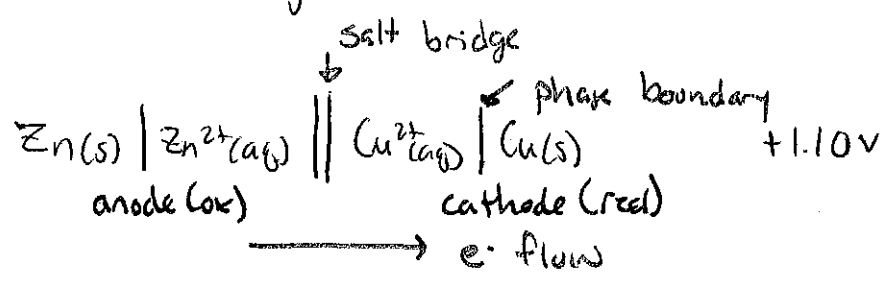
anode (-): ox



cathode (+): red

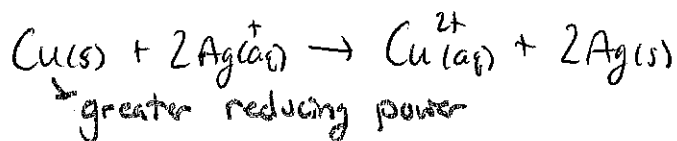
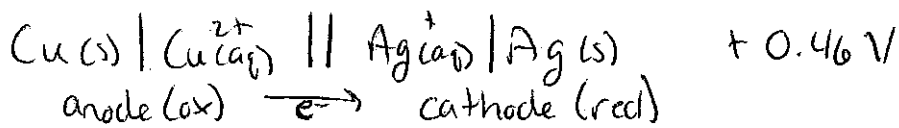
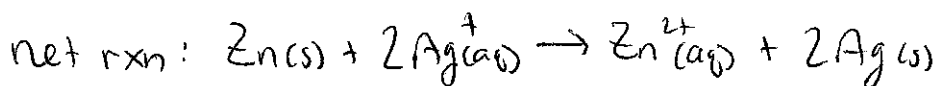
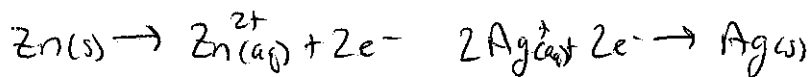
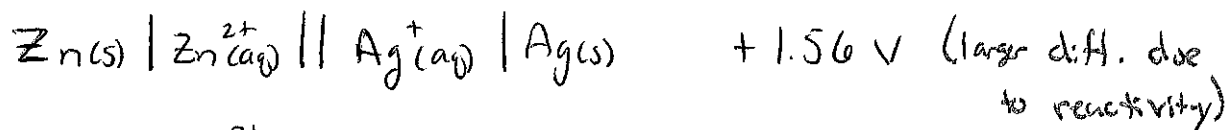


Simplified cell diagram



Diff. 1/2 cells make voltaic cells w/ diff. voltages
 direction of e- flow + voltage generated determined by diff in reducing strength

reactivity series



Standard Electrode Potentials (HL)

Units + terms used:

- amp (A) - SI unit for electric current (I)
- Coulomb (C) - SI unit for electric charge (Q)
(amt of charge transported in 1 sec by 1 amp)
eg: $Q = I \times t$ or $C = A \times s$ (units)
 $\text{e}^- = 1.602 \times 10^{-19} \text{ C}$
 $1 \text{ mol e}^- = 96,485.34 \text{ C mol}^{-1} \rightarrow \text{Faraday's (F) constant}$
- Volt (V) - SI unit of potential difference from 2 pts
 $V = J \times C^{-1}$ (amt of energy per Coulomb)
- Electromotive force (emf) \rightarrow greatest potential diff a cell can make (V)
cell potential (E_{cell})

emf created as e^- flow from (-) cell to (+) cell

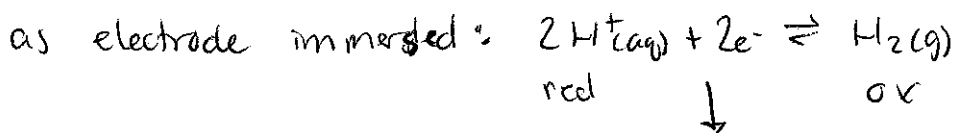
E_{cell} / electrode potentials difference = magnitude of V

based off relative reducing power

Standard hydrogen electrode (SHE) ← need reference pt.

Set up: $H_2(g)$ at 298K + 100 kPa
 (433) glass tube w/ holes to allow $H_2(g)$ to escape
 acid soln: 1 mol dm^{-3} $H^+(aq)$ → pH=0
 platinum electrode

inert metal → acts as catalyst for H^+ reduction
 coated in finely divide Pt, ↑ SA for
 ↑ absorption of $H_2(g)$



reversible depending on $\frac{1}{2}$ cell

• arbitrarily assigned '0' → when connected to another cell
 - any diff in V belongs to connected cell

Measuring Std electrode potentials

std $\frac{1}{2}$ cell conditions

conc: 1.0 mol dm^{-3}

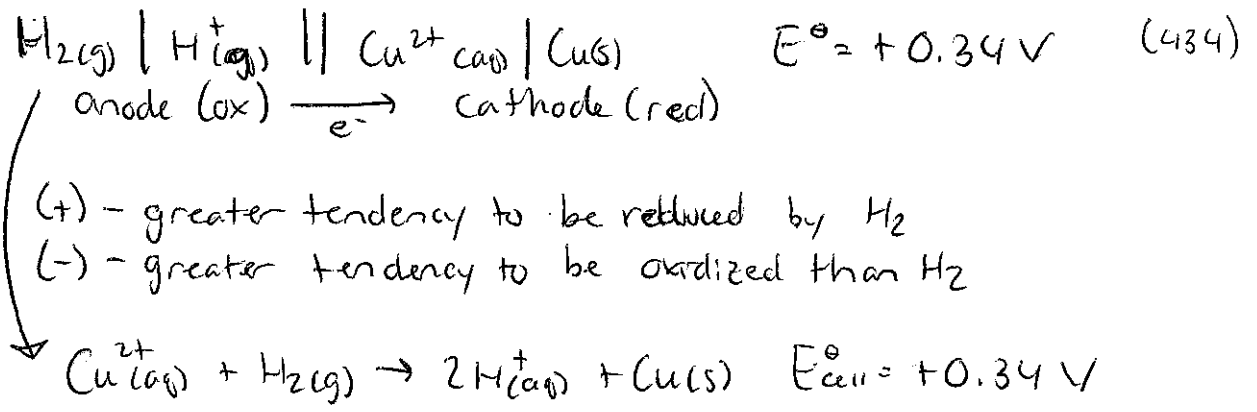
pressure: 100 kPa (if g)

pure substance

temp: 298K

$\frac{1}{2}$ cell does not include solid metal, Pt used

~~write~~ SHE + std 1/2 cell → complete circuit
 ↓
 emf generated = std electrode potential E^\ominus



More reactive metals lose e^- to reduce H^+ (435)

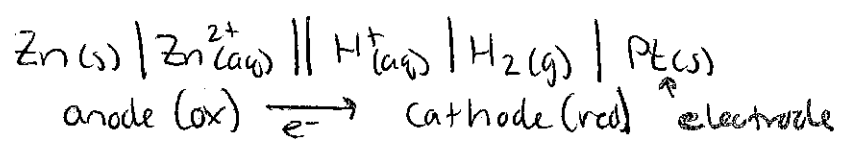
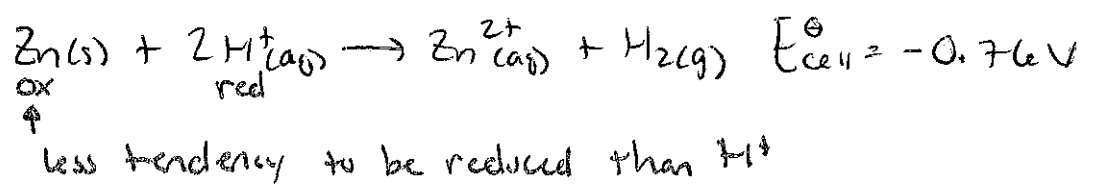


Table 24 E_{cell}^\ominus (std electrode potentials) → given for reduction rxn

When writing rxn oxidized sp \rightleftharpoons reduced sp.
 \uparrow due to eqm, set one way to read

- All E^\ominus values - red rxn
- E^\ominus do not depend on # of e^- (does not get scaled for stoichiometric eq)
- more positive E^\ominus , more readily reduced
and the (ox) more (-) $E^\ominus \rightarrow$ cathode (red) more (+) E^\ominus

Using E^\ominus data

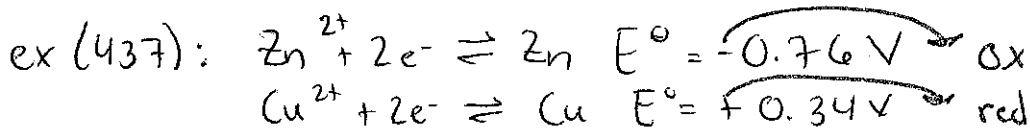
makes predictions about redox rxns & e^- flow direction (due to standardization)

1) Calculating cell potential, E_{cell}^\ominus

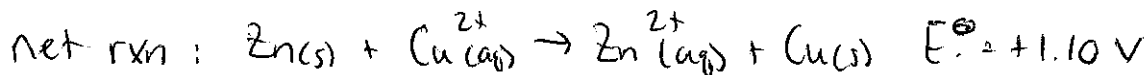
- from E^\ominus values: calculate emf for voltaic cell
deciding e^- flow - predict outcome of redox rxn

write
$$E_{\text{cell}}^\ominus = E_{\text{red cell}}^\ominus - E_{\text{ox cell}}^\ominus \quad (p-r)$$

- E^\ominus values must be reduction values
- E^\ominus are not multiplied by mole ratios



$$E_{\text{cell}}^\ominus = E_{\text{Cu}^{2+}}^\ominus - E_{\text{Zn}^{2+}}^\ominus = +0.34 - (-0.76) = +1.10 \text{ V}$$

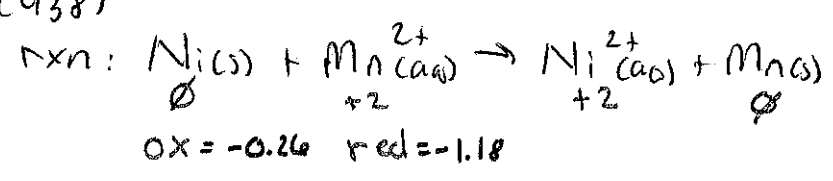


2) Determining spontaneity of a reaction

* substitute E^\ominus values into E^\ominus_{cell} equation based on how it is written

$E^\ominus_{\text{cell}} (+)$: spontaneous as written
 $E^\ominus_{\text{cell}} (-)$: non-spontaneous as written

ex: (438)



$$E^\ominus_{\text{cell}} = E^\ominus_{\text{Mn}^{2+}} - E^\ominus_{\text{Ni}^{2+}} = -1.18 - (-0.23) = -0.93 \text{ V (non-spont)}$$

Electrode potential & Free energy change (E^\ominus_{cell} & ΔG)

$$\Delta G^\ominus = -nFE^\ominus \quad \begin{matrix} n = \# \text{ moles } e^- \text{ transferred} \\ F = \text{faraday's constant} \end{matrix}$$

(Nernst eq)

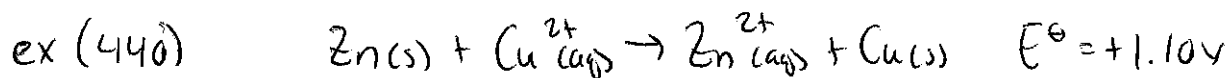
$$\Delta G^\ominus (\text{J}) = \cancel{n(\text{mol})} F(\text{C/mol}) E^\ominus (\text{V})$$

$\text{J} = \text{C} \times \text{V}$

E^\ominus & ΔG have opposite signs

$E^\ominus_{\text{cell}} (+)$: $\Delta G^\ominus (-)$ → spont
 $E^\ominus_{\text{cell}} (-)$: $\Delta G^\ominus (+)$ → non spont
 $E^\ominus_{\text{cell}} = \emptyset$: $\Delta G^\ominus = \emptyset$ → eqm

Voltmeter indirectly measures of free-energy as well as electrode potential (more + E^\ominus_{cell} , more spont)

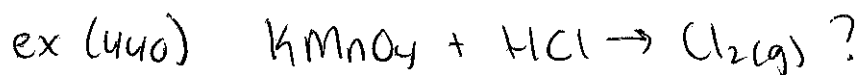


$$\begin{aligned} \Delta G &= -nFE^\ominus \\ &= -2(\text{mole } e^-) \times 96500(\text{Cmol}^{-1}) \times 1.10(\text{V}) \\ &= -212,000\text{J} \rightarrow -212\text{kJ} \end{aligned}$$

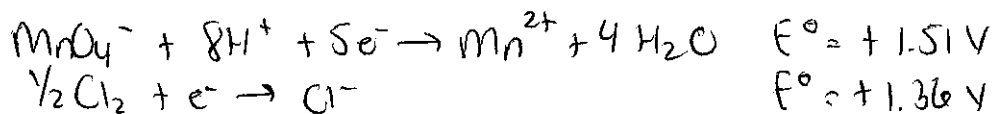
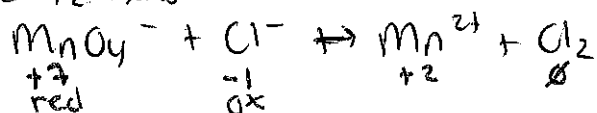
3) Comparing relative oxidizing & reducing power of $\frac{1}{2}$ cells

metals $\downarrow E^\ominus$ values - stronger reducing agent
non-metals $\uparrow E^\ominus$ values - stronger oxidizing agent

Table (440)



1) write $\frac{1}{2}$ rxns



$$E^\ominus_{\text{cell}} = E^\ominus_{\text{MnO}_4^-} - E^\ominus_{\text{Cl}_2} = +1.51 - (+1.36) = +0.15\text{V}$$

↓
Spontaneous
(does not determine
rate (441))

Electrolytic Cells (SL)

Voltaic cell: takes energy of spontaneous redox rxn & harnesses it to produce electric voltage

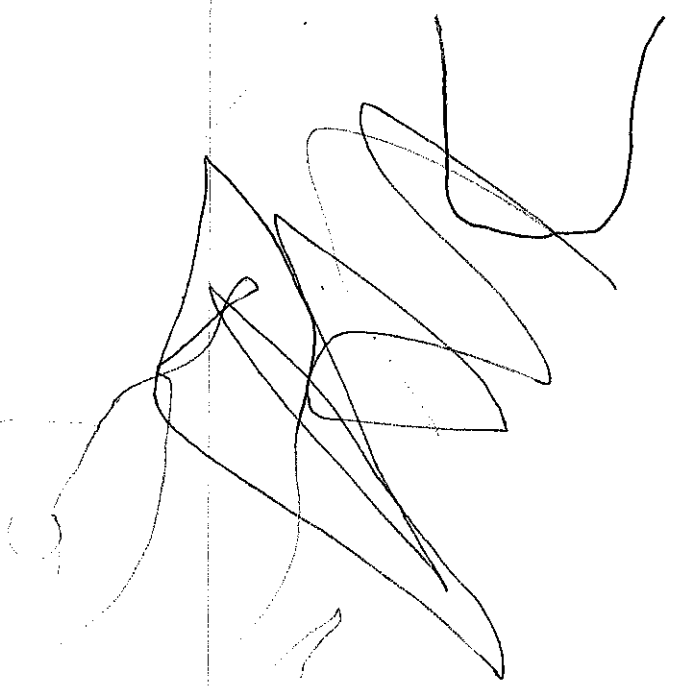
VS.

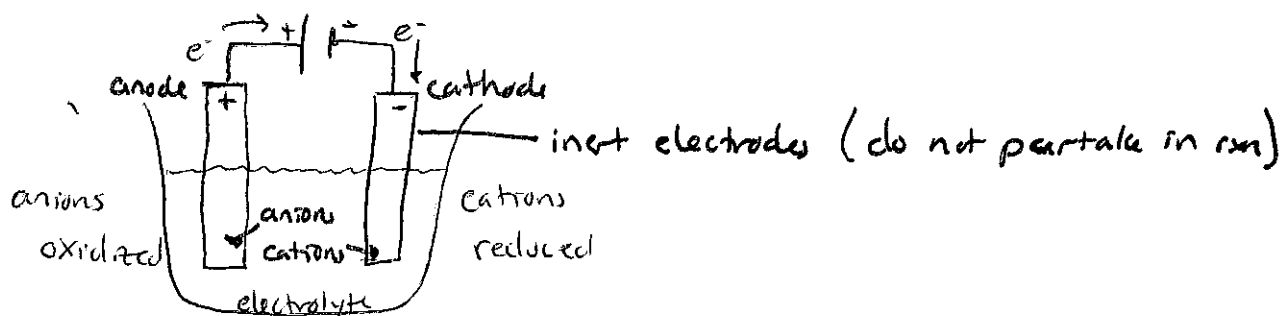
electrolytic cell: uses external source of voltage (electrical energy) to run a non-spontaneous redox rxn

electrolyte: reactant in process
(molten ionic compd / soln of ionic compd)

electric current → electrolyte → redox occurs at electrodes → remove charges on ions → creating neutral elements (discharged)

Purpose: separating important reactive metals from their ores





- Source of power: battery / DC current $\begin{matrix} + \\ - \end{matrix}$
- electrodes must be immersed into electrolyte & connected to power supply - made of conducting substance (metal / graphite)
- electric wires connect electrodes to power supply

Works:

power source pushes e^- to cathode (- electrode) \rightarrow
 neutralizes cations in electrolyte \rightarrow anions migrate
 to anode (+ electrode) \rightarrow donate e^- (neutralized) \rightarrow
 complete circuit \rightarrow neutral elements product

Redox Rxns occur at electrodes

- negative electrode (cathode): $M^+ + e^- \rightarrow M$ (reduced)
(+) ions attracted to (-) electrode)
 - positive electrode (anode): $A^- \rightarrow A + e^-$ (oxidized)
(-) ions attracted to (+) electrode)
- * nature of redox rxn defines electrodes (not charge)

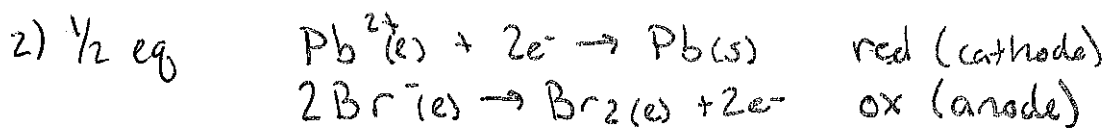
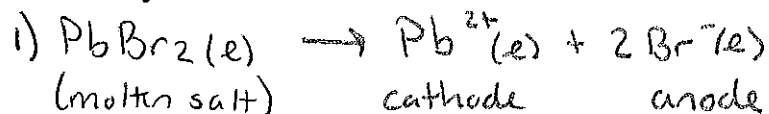
	Voltaic cell		Electrolytic cell	
anode	oxidation	-	oxidation	+
cathode	reduction	+	reduction	-

Predicting products in electrolytic cell

- 1) Identify all ions in electrolyte - determine migration
- 2) More than 1 ion at each electrode?
Determine discharge based off E° value (aq solns)
- 3) write $\frac{1}{2}$ eq for rxn at electrode
(e^- released at anode / taken up at cathode)
- 4) Balance e^- lost / gained to write net rxn
- 5) consider what changes would be observed

Electrolysis of Molten Salts \rightarrow only ions present is compound itself (no solvent)

ex (444)



4) observable changes anode: Brown l w/ strong smell
cathode: grey metal

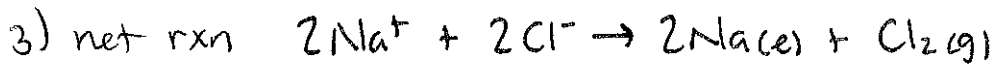
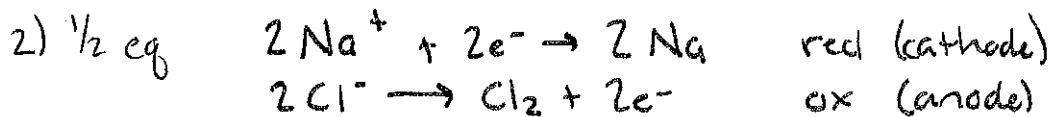
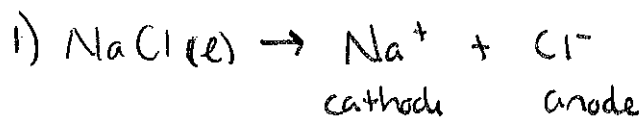
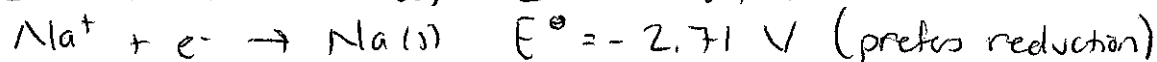
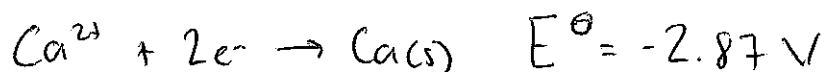
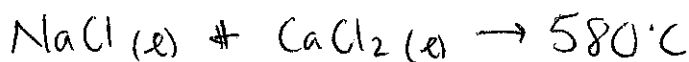
Problem w/ process is high melting pts of salts (expensive)

Soln: • mix 2 molten salts together - lowering melting pt of higher ~~melting~~ salt

• choose salt that lower E^\ominus value \rightarrow does not get reduced

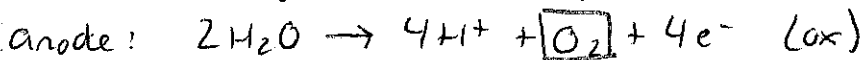
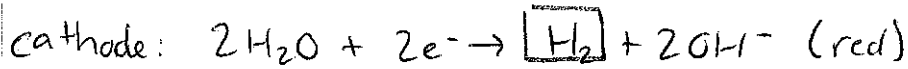
Problem #2: toxic by-products made (ethical issues)

ex (444) $\text{NaCl}(l) \rightarrow 801^\circ\text{C}$ melting pt.



Electrolysis of aqueous solns (HL)

- involves ions of water & ionic compound
- selective discharge \rightarrow only 1 of multiple ions get discharged



adding in M^+A^-

anode: A^- or H_2O oxidized

cathode: M^+ or H_2O reduced

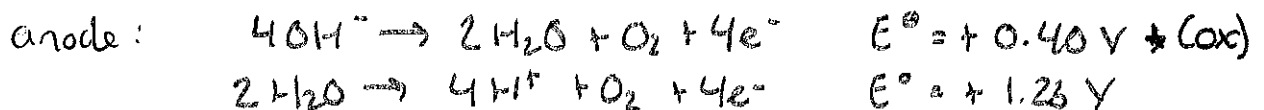
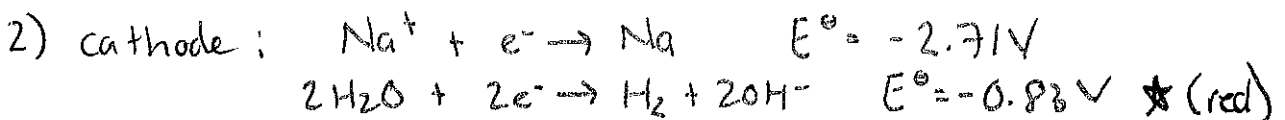
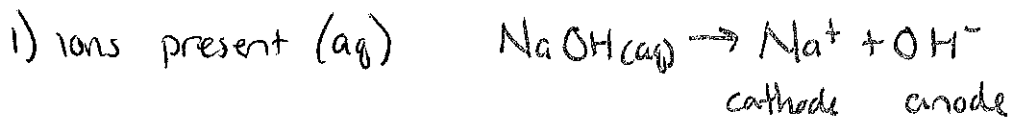


selective discharge occurs

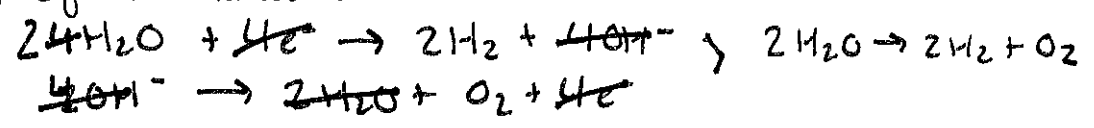
determined by: relative E^\ominus values of ions
 relative conc. of ions in electrolyte
 nature of electrodes

Electrolysis of water

b/c ionization of pure H_2O is low (1.0×10^{-14}) \rightarrow must add ions to inc. conductivity of water (ions must not interfere w/ ions of H_2O to work)



3) overall eq w/ balanced e⁻



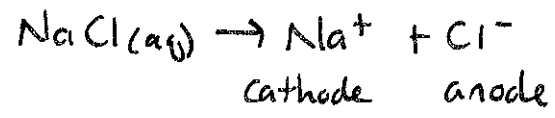
4) observed:

colorless gas at each electrode
 2:1 ratio. (stoichiometry)
 pH at anode ↓ as OH⁻ discharged
 pH at cathode ↑ as H⁺ discharged

Electrolysis of NaCl(aq) (Brine)

produces: H₂, Cl₂, NaOH (all commercially important)

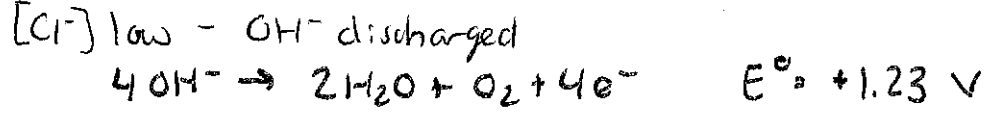
1) ions present:



2) cathode

refer to H₂O electrolysis (H₂O ox)

anode:

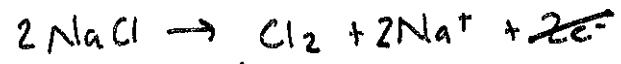


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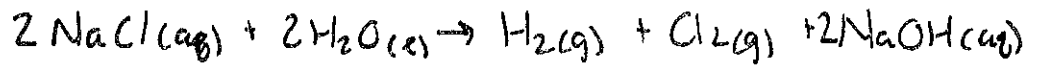
[Cl⁻] high - NaCl 28% by mass of soln - Cl⁻ discharged



3) overall eq w/ Cl⁻ discharged after balancing e⁻



↓



Copper electrodes (purpose: purify impure Cu metal)

2) cathode: Same as above

anode: Cu electrode is oxidized supplying e⁻, dissolving as Cu²⁺



3) net rxn: movement of Cu²⁺ produced at anode to cathode where it is discharged

4) observed: pink-brown at cathode (Cu)
disintegration of Cu anode
No pH change
No change in blue color

VS Factors affecting amount of production in electrolysis

depends on: quantity of electric charge
stoichiometry of 1/2 rxns

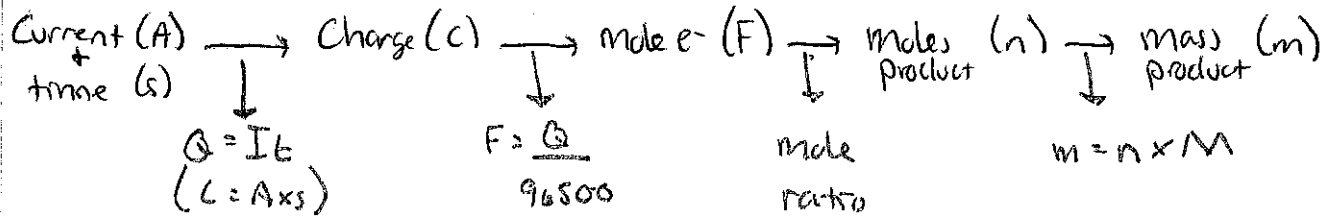
Quantify electric charge

Charge = current × time

$$Q(\text{C}) = I(\text{A}) \times t(\text{s})$$

$$(1 \text{ mole } \text{e}^{-} = 96,500 \text{ C})$$

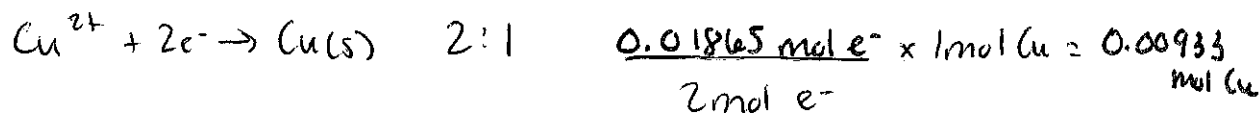
amt of product from redox



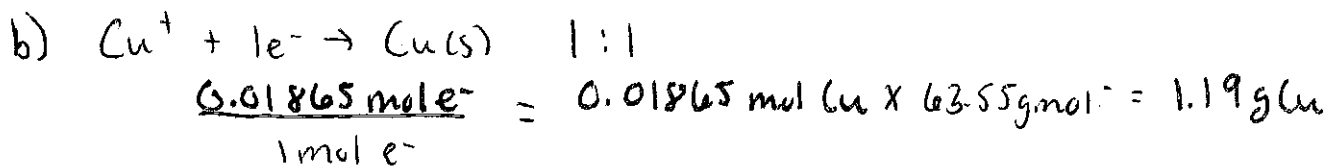
ex (452) Know: current = 2.00 A
 time = 15.0 mins
 ? g Cu from $\text{CuCl}_2(\text{aq})$

$$\text{a) } C = A \times t \rightarrow (2.00)(15.0 \times 60) = 1800 \text{ C}$$

$$F = \frac{1800 \text{ C}}{96500 \text{ C mol}^{-1}} = 0.01865 \text{ mol } e^{-}$$

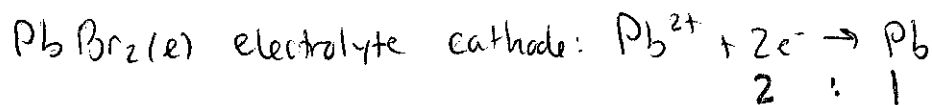
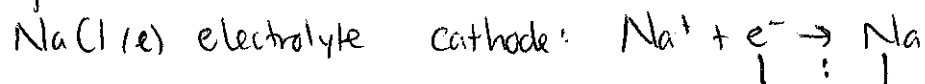


$$m = n \times M \quad 0.00933 \times 63.55 \text{ g mol}^{-1} = 0.593 \text{ g Cu}$$



Conclusion: ~~the~~ • charge on ion influences amt of product
 • current
 • duration of electrolysis

Compare:



Pb needs 2x more electricity to produce 1mol product

ex (454) know: current: 2.00 amps
 time: 10 mins
 amt: 0.0124 mol Ag formed

a) ? mol Ag, 1.00 A, 30 mins (ratio)

$$\frac{C_1}{C_2} = \frac{A_1 \times t_1}{A_2 \times t_2} \rightarrow C_2 = \frac{A_2}{A_1} \times \frac{t_2}{t_1} \times C_1$$

$$C_2 = 0.0124 \times \frac{1.00 \text{ A}}{2.00 \text{ A}} \times \frac{30 \text{ min}}{10 \text{ min}} = 0.0186 \text{ mol Ag}$$

b) Ag^+ vs. Cu^{2+} 1:2 e^- ratio
 $\frac{0.0186}{2} = 0.0093 \text{ mol Cu}$

Electroplating \rightarrow application of electrolysis

def: process of using electrolysis to deposit a layer of metal on top of another metal or conductive sub

features of electrolytic cell:

- 1) an electrolyte containing wanted metal ions to be deposited
- 2) cathode made of object to be plated
- 3) anode could be made of same metal so oxidation for replenishment can occur

Current & time are controlled for thickness

- purpose:
- 1) decorative (Ag silverware)
 - 2) corrosion control (galvanized iron)
 ↓
 sacrificial protection
 - 3) Improvement of function
 (Cr to protect steel tools)

Summary

Voltaic: convert chemical energy to electrical when rxn has (+)E value (goes towards eqm)

electrolytic: convert electrical energy to chemical when current drives rxn w/ (-)E value away from eqm

	E_{cell}	ΔG	
Voltaic	> 0	< 0	spontaneous
electrolytic	< 0	> 0	non-spont
eqm	0	0	dead battery