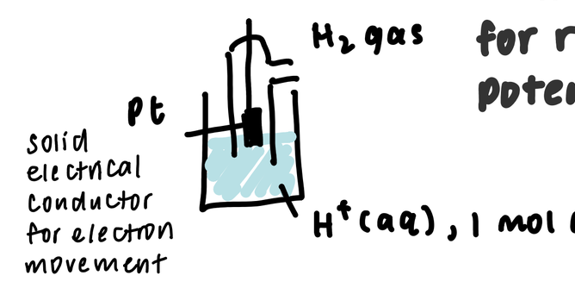
Electrochemistry
relationship between chemical reactions and electricity

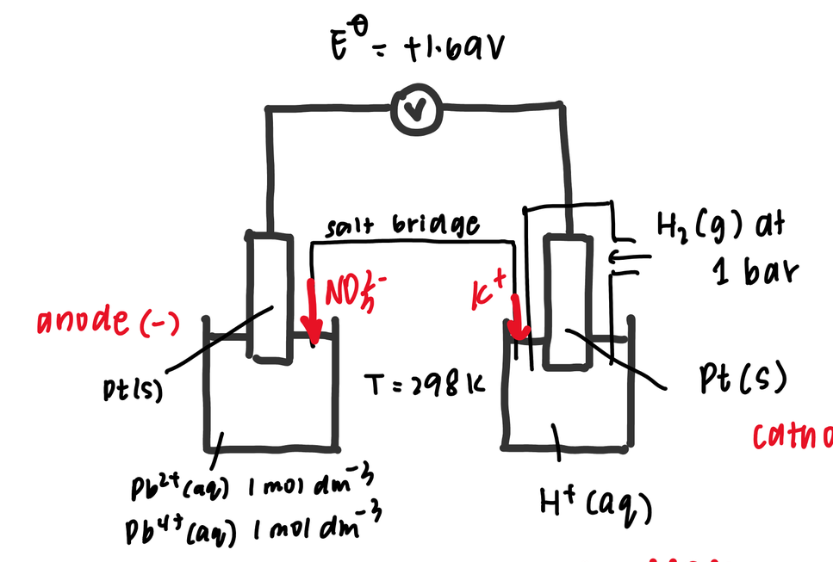
↗ does not account for solubility

Standard hydrogen electrode (SHE)
measures $E^\ominus$

↳ an electrode scientists use for reference on all half-cell potential reactions

↳ Arbitrarily assigned standard electrode potential of +0.00V





oxidation half cell
$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$
(K^+ to 'replenish' (+))

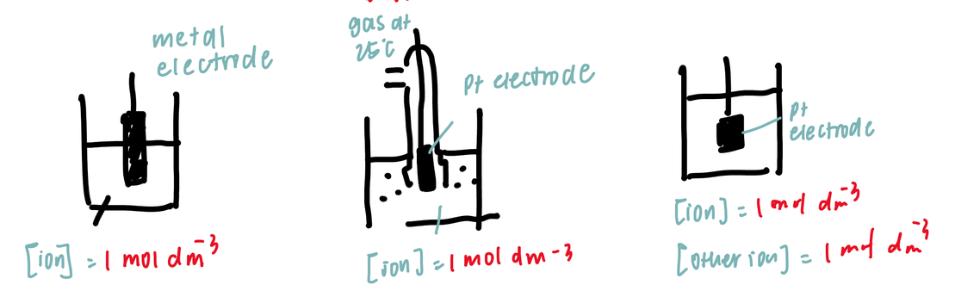
reduction half cell
$H_2 \rightarrow 2H^+ + 2e^-$

Standard conditions
$H_2(g)$ at 1 bar, 1 mol dm^{-3} H^+
298K
1 bar Pa for gases ONLY

$E^\ominus > 0$ reduction ($H_2(g) \rightarrow 2H^+(aq) + 2e^-$)
$E^\ominus = 0$ no net redox reaction → rea @ same rate)
$E^\ominus < 0$ oxidation ($2H^+(aq) + 2e^- \rightarrow H_2(g)$)
↳ more negative $E^\ominus$ = more reactive

SHE → half cell (-) ox
half cell → SHE (+) re

Half cells
1) metal in aq
2) non-metal in aq
3) ions of same element



$E^\ominus$ not to be scaled

Electrode potential: potential difference between metal and a solution of its ions at equilibrium (E)

$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$

↳ caused by charge separation across metal – solution surface
↳ (+) or (-) depending on the relative ease the metal loses electrons

Standard electrode potential ($E^\ominus$)
- likelihood of reduction
- emf / potential difference measured under standard conditions between a half cell and standard hydrogen electrode

Oxidising agent	Reducing agent
Gets reduced	Gets oxides
More positive the E value	More negative the E value
More favourable -> greater tendency to reduce	More favourable -> greater tendency to sidles
Stronger strength of oxidising agent	Stronger strength of reducing agent

Determining cell reaction
1) write $E^\ominus$ half cell
- more (+) → reduced → oxidising agent
- more (-) → oxidized → reducing agent

$E^\ominus_{cell} = E^\ominus_{reduction\ reaction} - E^\ominus_{oxidation\ reduction}$
↳ potential difference of 2 half cells measured under standard conditions

Spontaneous redox reactions
→ no need to give energy it'll happen $E^\ominus > 0$

$E^\ominus_{cell} > 0$ spontaneous
$E^\ominus_{cell} = 0$ no net redox reaction
$E^\ominus_{cell} < 0$ non-spontaneous, need battery

Can zinc react with $CuCl_2$?

1) Species present
Zn, Cu^{2+}, Cl^-, H_2O → metal displacement reaction

possible

reduction	oxidation
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ (+0.34V)	$Zn \rightleftharpoons 2e^- + Zn$ (-0.76V)
$Cu^{2+} + e^- \rightleftharpoons Cu^+$ (+0.15V)	$2Cl^- \rightleftharpoons Cl_2 + 2e^-$ (1.36V)
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ (-0.83V)	$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$ (1.23V)

2) Get most (+) / (-)
$E^\ominus_{cell} = +0.34 - (-0.76)$
$= +1.10V$
(>0)

$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ (water reduced)
(-0.83V)

KCr_2O_7 in Fe_2SO_4
K^+, $Cr_2O_7^{2-}$, Fe^{2+}, SO_4^{2-}, H_2O
possible

reduction
$K^+ + e^- \rightleftharpoons K$ (-2.93V)
$Fe^{2+} + 2e^- \rightleftharpoons Fe$ (-0.44V)
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + H_2O$ (1.33V)
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ (-0.83V)

oxidation
$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$ (+0.77V)
$2SO_4^{2-} \rightleftharpoons S_2O_8^{2-} + 2e^-$ (+2.01V)
$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$ (+1.23V)

$E^\ominus = 1.33 - 0.77$
$= 0.56V$

Electrochemical cell (galvanic / voltaic cell)
measuring $E^\ominus$

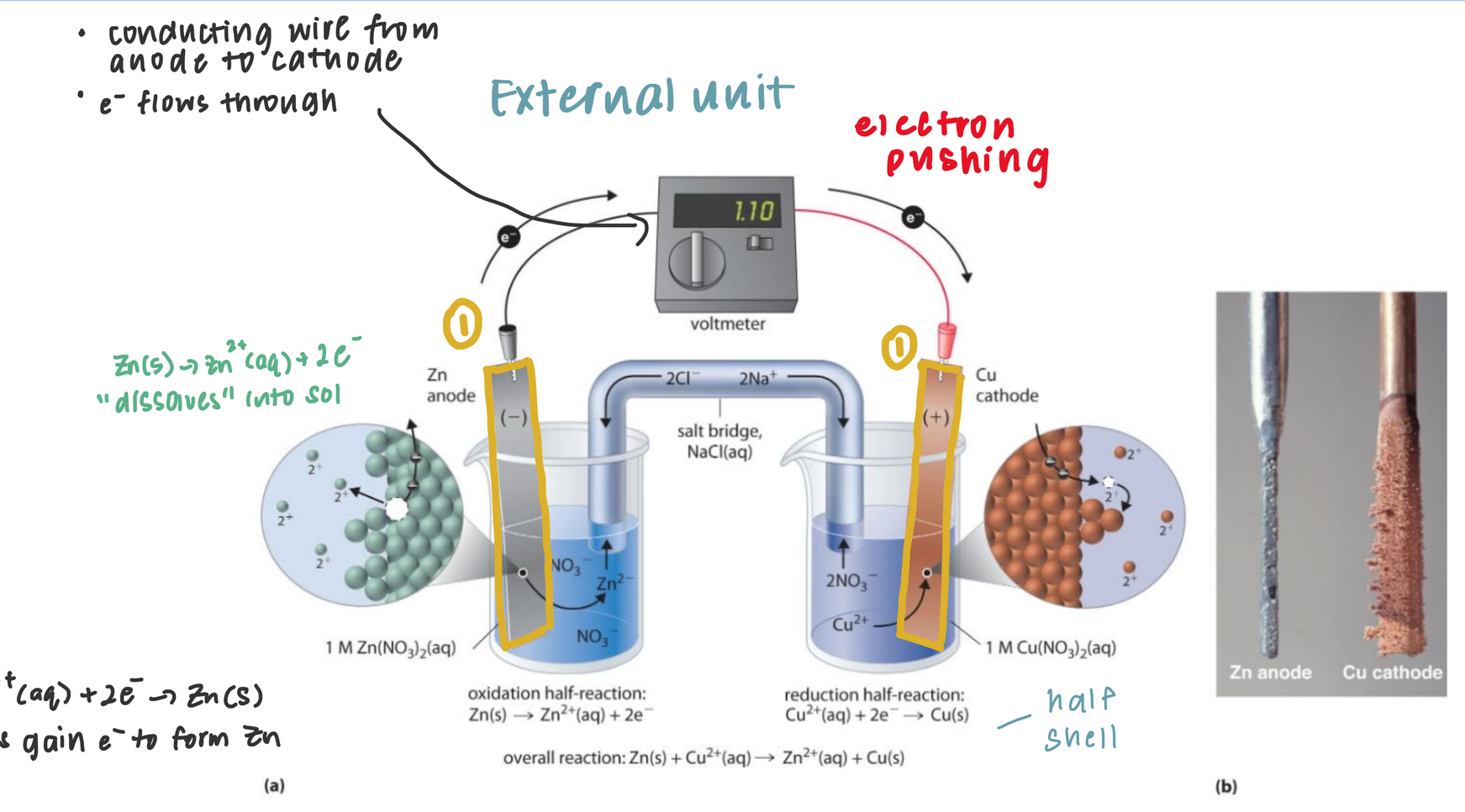
Spontaneous
$E^\ominus > 0$
1) e^- moves on its own
2) produces electricity (movement of e^-)

chemical E → electrical E

* If in same beaker
as e^- is directly transferred without an external wire. (exothermic)
chemical E → thermal E

anode → cathode
(+) (-)

- conducting wire from anode to cathode
- e^- flows through



▲ look at $E^\ominus$ vals to see which is the reduction half cell

reactive: $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$
less reactive: $Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2e^-$

Components
① **Electrode**
- electrical conductor
- allows for the movement of e^-

(+) — electrode is positive • electrons are used up here	Cathode: reduced, gain e^-	(-) give e^- to cations
(-) build up of (-) charges — electrode is negative • electrons are released here	Anode: oxidized, lose e^-	(+) give e^- to anions

- chemical reactions take place at the electrode
- electrolyte decomposed

Electrode
1) inert
↳ graphite
↳ platinum
• use when $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (both ions)

2) reactive → participates in redox reaction
↳ all other metals

② **Electrolyte**
- substance contains mobile e^- (can conduct electricity)
- to create equilibrium
• create a layer around anode and cathode

③ **Salt Bridge**
- maintaining electrical neutrality
- prevents build up charges
(lets e^- flow easily)

"cations" flow to the cathode
$Fe^{3+} \rightarrow Fe^{2+} + e^-$, Fe^{3+} gets less positive so Na^+ ions are supplied

"anions" flow to the anode
$Cu^{2+} + 2e^- \rightarrow Cu$, Cu^{2+} gets more positive so NO_3^- ions are supplied

Electrolytic cell
Electrolysis

non-spontaneous
requires E to occur
electrical E → chemical E

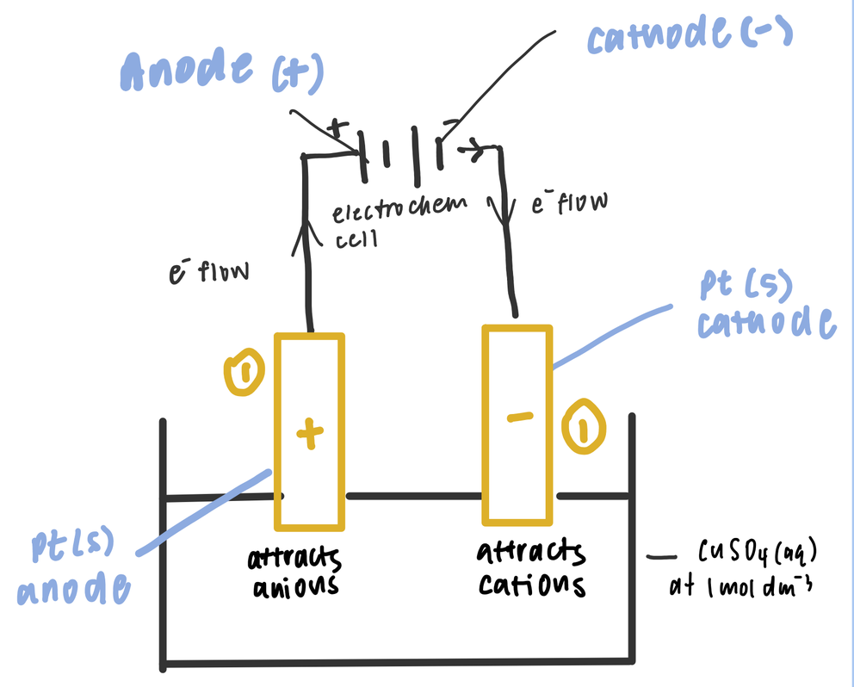
cathode → anode
(-) (+)

▲ anion → anode (+)
cation → cathode (-)

Look at $E^\ominus$ to determine which is oxidised / reduced → consider electrode

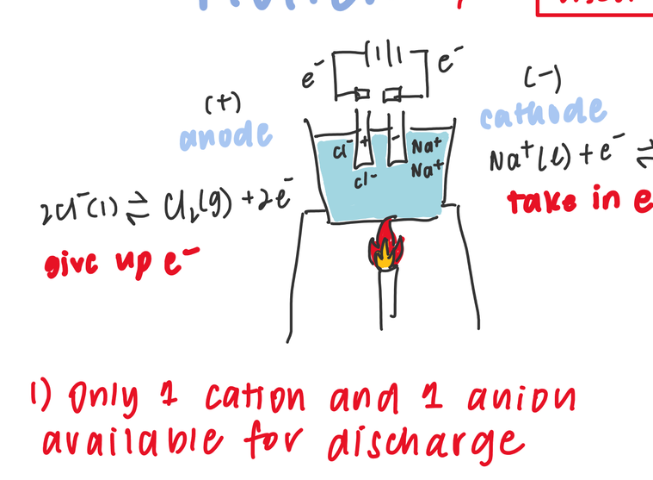
polarities of electrodes are reversed

Battery
provides source of e^- flowing in a direction



anode → cathode

Molten
→ inert electrodes used for electrolysis



1) Only 1 cation and 1 anion available for discharge

For aqueous:
anode (oxidation)
$2H_2O(l) \rightleftharpoons O_2(g) + 4H^+(aq) + 4e^-$
$E^\ominus = +1.23V$
O_2 is produced

cathode (reduction)
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$
$E^\ominus = -0.83V$
H_2 is produced

Discharge
- process of gaining / losing e^- at the electrodes
- when ions are discharged
⇒ forms atoms / molecules

Selected discharge
→ includes H_2O

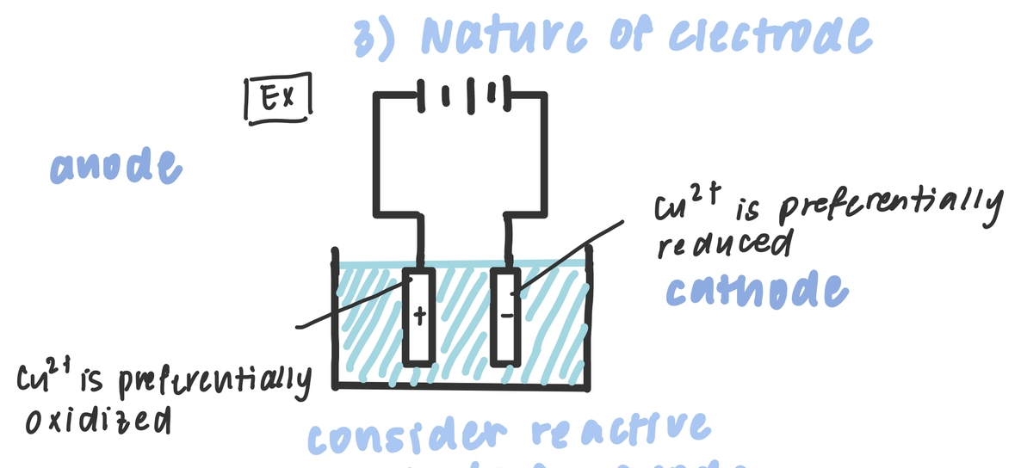
1) Ease of oxidation / reduction
At (+) electrode (anode): easiest to oxidize (smaller $E^\ominus$)
At (-) electrode (cathode): easiest to be reduced (larger $E^\ominus$)

2) concentration of species
higher conc discharged in preference of lower conc
↳ if $E_A^\ominus < E_B^\ominus$ (not large) but $conc_A > conc_B$
A is reduced

• dilute : more water

3) Nature of electrode

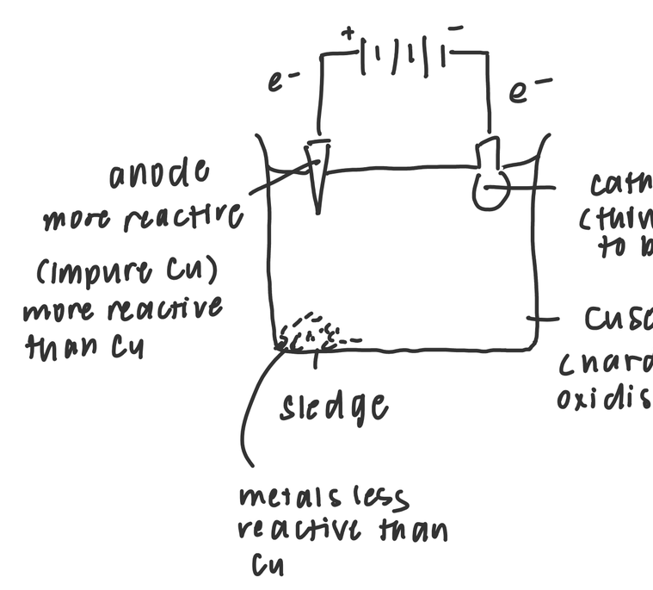
Ex



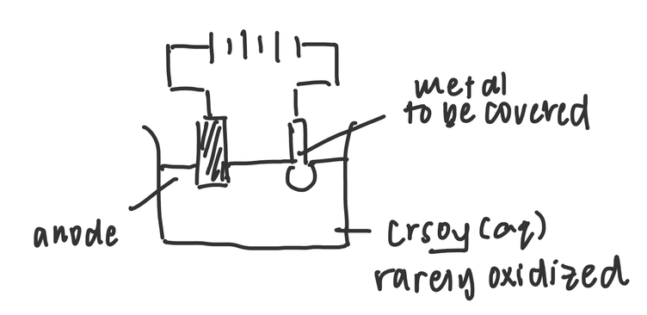
consider reactive electrode for anode and cathode
• replenishing

Industrial applications of electrolysis

1) Electric purification of copper



2) Electroplating
- depositing a layer of metal onto another metal



$Q = I \times t$

Faraday's 1st law of Electrolysis
more electricity → more gas / solid liberated

Faraday's 2nd law of Electrolysis
qty of electricity required to discharge 1 mol of an element depends on the charge on the ion

Faraday constant
$F = (6.02 \times 10^{23})(1.60 \times 10^{-19})$ → charge
↳ Avodagro constant
$= 96500C$ or 1 Faraday

$Q = F \times n_e$
Q: charge (C)
F: Faraday constant (F)
n_e: amt of e^- (mol)

n_e = # of mols of e^-