Electrochemistry

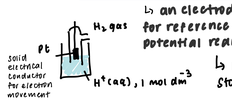
Thursday, April 10, 2025 10:59 AM

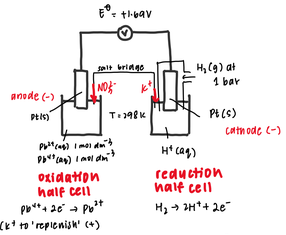
measures $E^\ominus$

## Standard hydrogen electrode (SHE)

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

↳ Arbitrarily assigned standard electrode potential of +0.00V




### Standard conditions

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

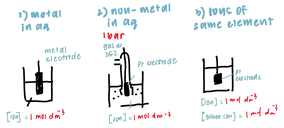
$E^\ominus > 0$ reduction ($H_2$(g) → $2H^+$(aq) + $2e^-$)
$E^\ominus = 0$ no net redox reaction → reaction at same rate
$E^\ominus < 0$ oxidation ($2H^+$(aq) + $2e^-$ → $H_2$(g))

↳ more negative $E^\ominus$ = more reactive

$E^\ominus$ not to be scaled

## Half cells

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




**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

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

## 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 (+ve) to 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) | $Zn \rightleftharpoons 2e^- + Zn^{2+}$ (-0.76V) |
| $Cu^{2+} + e^- \rightleftharpoons Cu^+$ (+0.40V) | $2Cl^- \rightleftharpoons Cl_2 + 2e^-$ (1.36V) |
| $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ (-0.83V) | $2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$ (1.22V) |

2) 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 $Fe_2(SO_4)_3$

$K^+$, $Cr_2O_7^{2-}$, $Fe^{2+}$, $SO_4^{2-}$, $H_2O$

possible

| reduction | oxidation |
|---|---|
| $K^+ + e^- \rightleftharpoons K$ (-2.93V) | $Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$ (+0.77V) |
| $Fe^{3+} + 2e^- \rightleftharpoons Fe$ (-0.44V) | $2SO_4^{2-} \rightleftharpoons S_2O_8^{2-} + 2e^-$ (+2.01V) |
| $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + H_2O$ (1.33V) | $2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$ (+1.23V) |
| $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ (-0.83V) | |

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

## Electrochemistry

relationship between chemical reactions and electricity

↗ does not account for solubility

measuring $E^\ominus$

### Electrochemical cell (galvanic / voltaic cell)

* if in same beaker

**Spontaneous** $E^\ominus > 0$

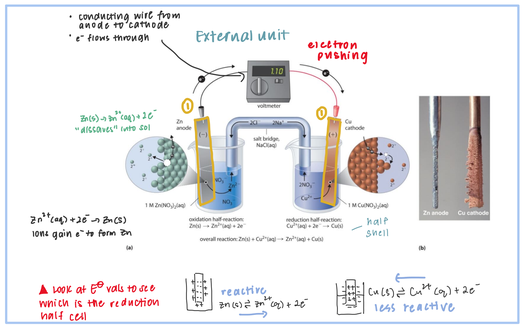
1) $e^-$ moves on its own
2) produces electricity (movement of $e^-$)

as $e^-$ is directly transferred without an external wire.

Chemical E → thermal E (exothermic)

anode → (+) cathode (-)

Chemical E → electrical E




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

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

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

polarities of electrodes are reversed

### Components

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

(+) Cathode
- electrode is positive
- electrons are used up here

reduced
gain $e^-$

(-) Anode
build up of (-) charges
- electrode is negative
- electrons are released here

Oxidized
lose $e^-$

(-) give $e^-$ to cations

(+) give $e^-$ to anions

- chemical reactions take place at the electrode
- electrolyte decomposed

Electrode
1) inert
↳ graphite
↳ platinum
• not used
$Fe^{3+}/Fe^{2+}$ (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 $NO_3^-$ 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

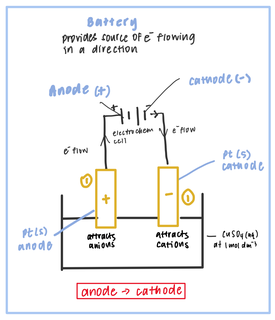
Cathode → anode (-) (+)

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

look at $E^\ominus$ to determine which is oxidized / reduced → consider electrode

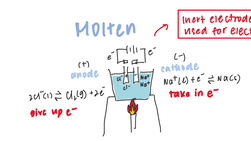
### Battery

provides source of $e^-$ flowing in a direction




### 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) | At (-) electrode (cathode) |
|---|---|
| Easiest to oxidise (smaller $E^\ominus$) | Easiest to be reduced (larger $E^\ominus$) |

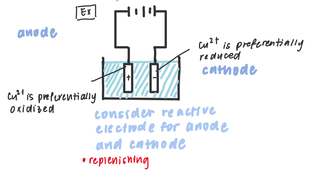
2) concentration of species

higher conc discharged in preference of lower conc

↳ If $E^\ominus_A < E^\ominus_B$ but $conc_A > conc_B$ (even large)
A is reduced

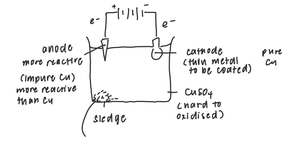
• dilute : more water

3) Nature of electrode

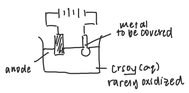



## Industrial applications of electrolysis

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

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

$n_e$ = # of mols of $e^-$