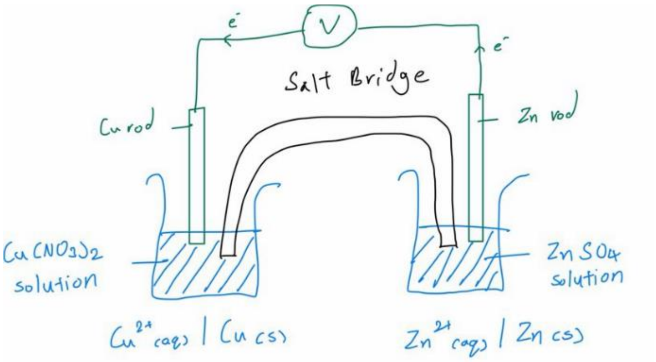
Electrochemical Cells



Reactions

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ — Reduction — Cathode

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ — Oxidation — Anode

Note: Salt bridge is meant to prevent mixing of both solutions in both half cells but still let ions pass through. Also meant to keep solutions electrically neutral, so there is no buildup of charges which could lead to reactions stopping.

Electrode Potential

$M^{n+}_{(aq)} + ne^- \rightleftharpoons M_{(s)}$ $\quad E(M^{n+}_{(aq)} | M_{(s)})$

Positive E ⇒ POE lies to right
↳ Reduction Favoured

Negative E ⇒ POE lies to left
↳ Oxidation Favoured

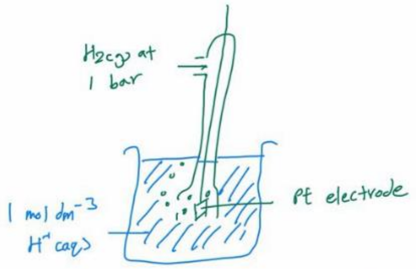
Factors affecting Electrode Potential

- Note: Refer to Chemical Equilibria Masterclass
  - All the reactions are reversible
  - Factors that affect POE would affect the Electrode Potential
- Concentration of ions
- Temperature
- Pressure of Gas

Standard Electrode Potential: E° is the relative potential of electrode under standard conditions compared to the standard hydrogen electrode that has an assigned 0 V.

Standard Hydrogen Electrode consists of H_2 (g) at 1 bar bubbling over platinum electrode coated with finely divided platinum which is dipped into 1 mol dm^{-3} H^+ (aq).

Standard Hydrogen Electrode (S.H.E.)



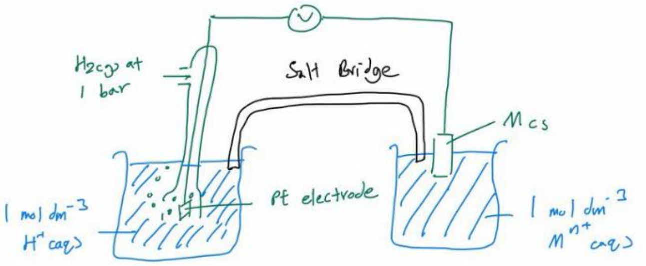
$E^{\circ}(H^+_{(aq)} | H_{2(g)}) = 0 V$

Reaction

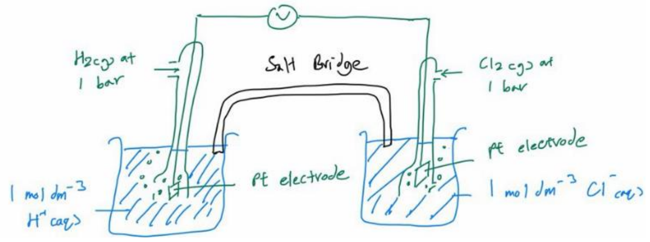
$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$

Measuring E°

- Remember: Everything must be in standard conditions
- Solutions at 1 mol dm^{-3}
- Gases at 1 bar pressure
- Electrode is platinum unless there is a metal solid involved
- Temperature at 298K
- Note: you MUST know how to draw

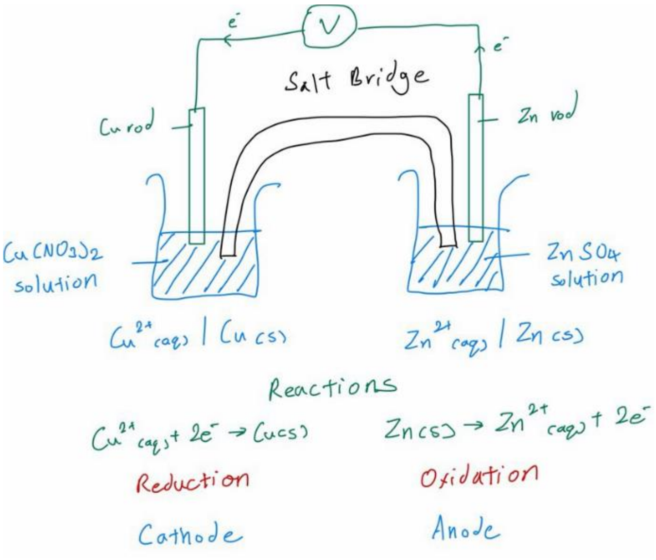


For half cells with gases



Cell Notations

Notation used	Meaning
|	Boundary btwn 2 phases in contact
||	Salt bridge
,	2 oxidation states sharing the same homogenous aqueous phase



From the above we can decipher the cell notation:

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

The anode has to be on the left, and the cathode on the right.

Note: If you use a non-metal in your half-cell, you would need to use a Pt electrode

e.g.

- Pt(s) | H_2 (g) | H^+ (aq) || ..
- .. || Fe^{3+}(aq), Fe^{2+}(aq) | Pt(s)

<u>Standard Cell Potential</u>: E°cell is the e.m.f of an electrochemical cells that consists of 2 half-cells under standard conditions. The E°cell value is the difference between the 2 standard electrode potentials

Calculating E°cell

$$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$$

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

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^\ominus = -0.76\,V$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^\ominus = +0.34\,V$$

$$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox} = +0.34 - (-0.76)$$
$$= +1.10\,V$$

Predicting Feasibility of Reaction with E°

Feasibility of Redox Reaction.

$E^\ominus_{cell} > 0\,V$: Spontaneous

$E^\ominus_{cell} < 0\,V$: Not Spontaneous

$E^\ominus_{cell} = 0\,V$: Equilibrium Established

Limitation of Standard electrode Potential

- E° tells feasibility of reaction but not the rate of reaction (Hint: Similar to ΔG)
- E° requires standard conditions. Any change in factors which affect POE would affect E

Relationship between ΔG and E

$$\underbrace{\Delta G^\ominus}_{J\,mol^{-1}} = -nFE^\ominus$$

F = Faraday Constant = 96500 $C\,mol^{-1}$

Development of Improved Batteries

- Going towards a trend of smaller size, lower mass, higher volage, lower cost, long shelf life