Electrochemistry

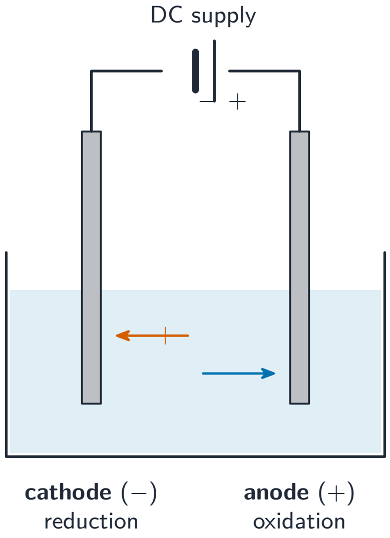
A-Level Chemistry

Electrolysis

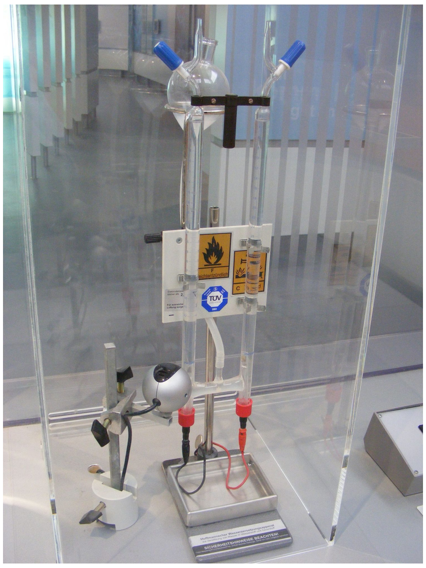
Electrolysis 电解 uses electricity to break down a molten or aqueous **electrolyte** 电解质. Positive ions move to the negative electrode and negative ions move to the positive electrode.

At each **electrode** 电极 a half-reaction happens:

- at the **cathode** 阴极 (negative): positive ions gain electrons (reduction).
- at the **anode** 阳极 (positive): negative ions lose electrons (oxidation).



Electrolysis: the DC supply drives positive ions to the cathode (reduction) and negative ions to the anode (oxidation)



A Hofmann voltameter for the electrolysis of water: the power supply drives current through two electrodes, and the gas made at each one collects in its side tube

Image: Mattes, CC BY-SA 3.0 (commons.wikimedia.org)

Predicting the products

- a **molten** electrolyte gives the metal at the cathode and the non-metal at the anode.
- an **aqueous** electrolyte also contains water. At the cathode, a less reactive metal is released, but for a reactive metal you get hydrogen instead. At the anode you usually get oxygen, but a concentrated halide solution gives the halogen.

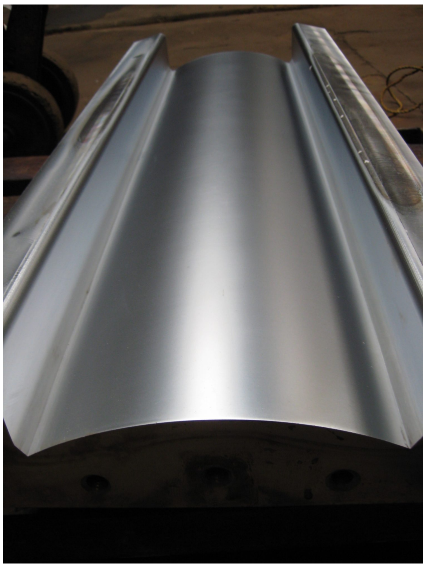
Calculations

The charge on one mole of electrons is the **Faraday constant** 法拉第常量, linked to the **Avogadro constant** 阿伏伽德罗常量 (L) and the charge on one electron (e) by $F = Le$.

The charge passed is $Q = It$ (current × time). Then:

1. moles of electrons $= Q/F$.
2. use the half-equation to find moles of product.
3. find the mass ($\times M_r$) or the gas volume.

Measuring the mass deposited for a known charge lets you work back to a value of the Avogadro constant.



Electrolysis is used to electroplate an object with a thin, shiny layer of metal such as chromium

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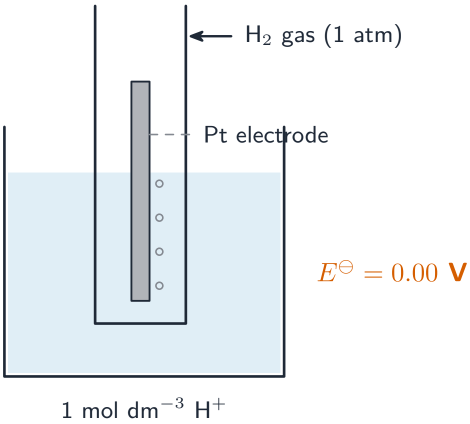
Standard electrode potentials and cell potentials

The **electrode potential** 电极电势 (E) of a half-cell shows how easily it is reduced. We measure it against a reference, under standard conditions, to get the **standard electrode potential** 标准电极电势 ($E^\ominus$), always written as a reduction.

The reference is the **standard hydrogen electrode** 标准氢电极: hydrogen gas at 1 atm over platinum in 1 mol dm^{-3} H$^+$, defined as exactly 0.00 V.



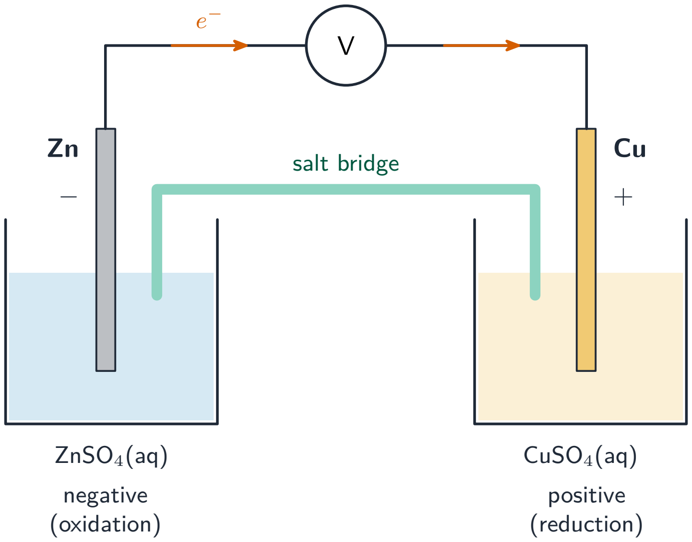
The standard hydrogen electrode: H_2 at 1 atm over platinum in 1 mol dm^{-3} H^+, the 0.00 V reference for every electrode potential

To measure an $E^\ominus$, connect the half-cell to the standard hydrogen electrode and read the voltage. A metal sits in a solution of its ions; for two ions of the same element (such as Fe^{3+}/Fe^{2+}), a platinum electrode dips into a solution containing both.

Combining half-cells

The **standard cell potential** 标准电池电势 is the difference between the two standard electrode potentials:

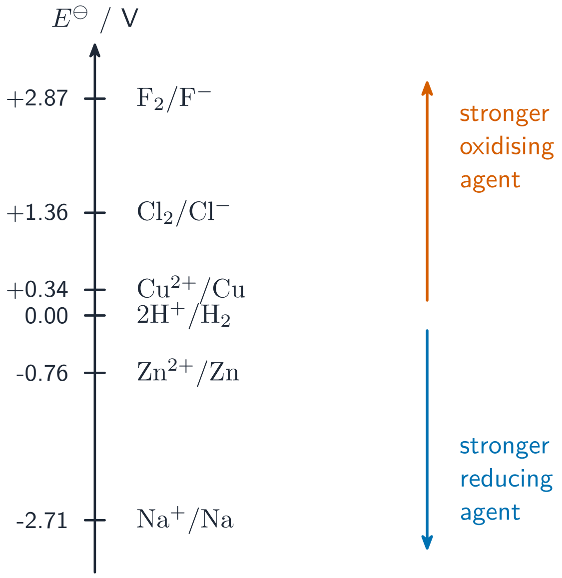
$$E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{more positive}) - E^{\ominus}(\text{less positive})$$



A simple cell: two half-cells joined by a salt bridge, with a voltmeter. Electrons flow from the negative (Zn) electrode to the positive (Cu)

From $E^{\ominus}$ values you can:

- find the **polarity**: the more negative electrode is the negative terminal, and electrons flow from it through the external circuit to the positive electrode.
- judge **reactivity**: a more positive $E^{\ominus}$ means a better **oxidising agent** 氧化剂 (easily reduced); a more negative $E^{\ominus}$ means a better **reducing agent** 还原剂.



The electrochemical series: a more positive $E^\ominus$ (top) is a stronger oxidising agent; a more negative $E^\ominus$ (bottom) is a stronger reducing agent

Feasibility and redox equations

A reaction is feasible when $E^\ominus_{\text{cell}}$ is **positive**. To build the full equation, take the two **half-equations** 半反应方程式, reverse the one that is oxidised, and add them so the electrons cancel. This $E^\ominus$ test tells you the **feasibility** 可行性 of the reaction.

You can also link it to free energy: $\Delta G^\ominus = -nE^\ominus_{\text{cell}}F$, where n is the moles of electrons.

The Nernst equation

If the concentrations are not standard, the electrode potential changes. Raising the concentration of the **oxidised** species makes E more positive. The **Nernst equation** 能斯特方程 gives the exact value:

$$E = E^\ominus + \frac{0.059}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

where z is the number of electrons in the half-equation.