Electrochemistry

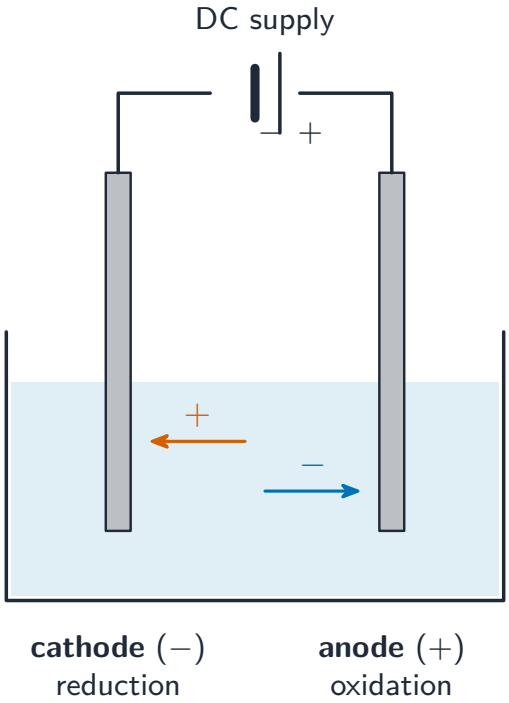
A-Level Chemistry

Electrolysis

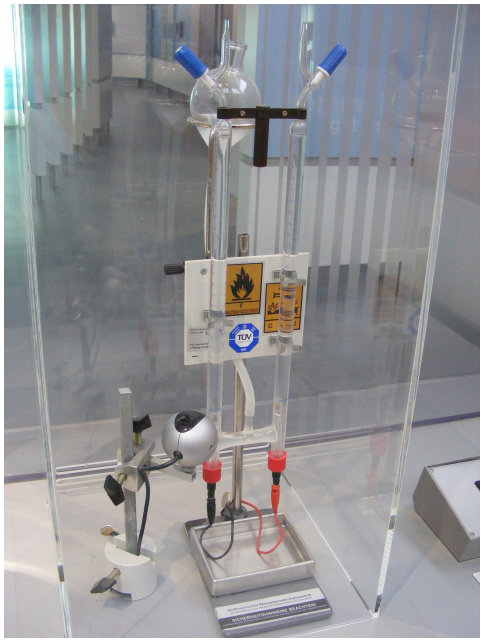
Electrolysis 电解 uses electricity to break down a molten or aqueous **electrolyte** 电解质. Positive ions move to the negative electrode and negative ions move to the positive electrode.

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

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.

molten
metal at cathode
non-metal at anode

aqueous
also contains water,
so H_2 or O_2 may form

A molten electrolyte gives the metal and non-metal; aqueous also has water

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 $\times$ time). Then:

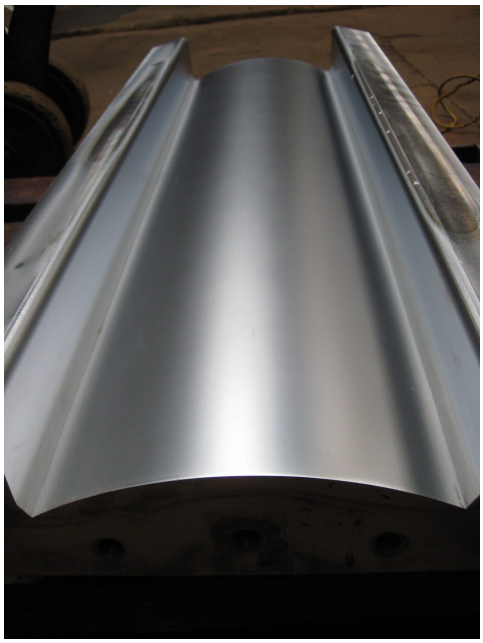
1. moles of electrons $= Q/F$.
2. use the half-equation to find moles of product.
3. find the mass ($\times M_r$) or the gas volume.

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

Worked example. A current of 2.0 A flows for 30 minutes through copper(II) sulfate solution, depositing copper at the cathode: $Cu^{2+} + 2e^- \rightarrow Cu$. Find the mass of copper deposited. ($F = 96\,500$ C mol^{-1}, A_r Cu $= 64$.)

Charge passed: $Q = It = 2.0 \times (30 \times 60) = 3600$ C. Moles of electrons $= Q/F = 3600/96\,500 = 0.0373$ mol. From the half-equation, 2 mol of electrons give 1 mol of Cu, so $n(\text{Cu}) = 0.0187$ mol and

$$m = nM = 0.0187 \times 64 \approx 1.2 \text{ g}.$$

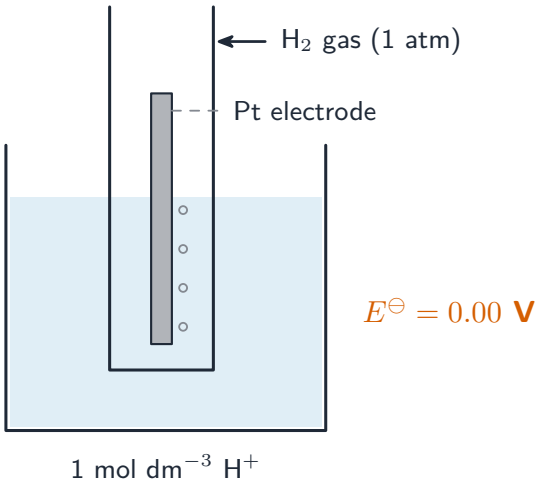


Electrolysis is used to electroplate an object with a thin, shiny layer of metal such as chromium

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.



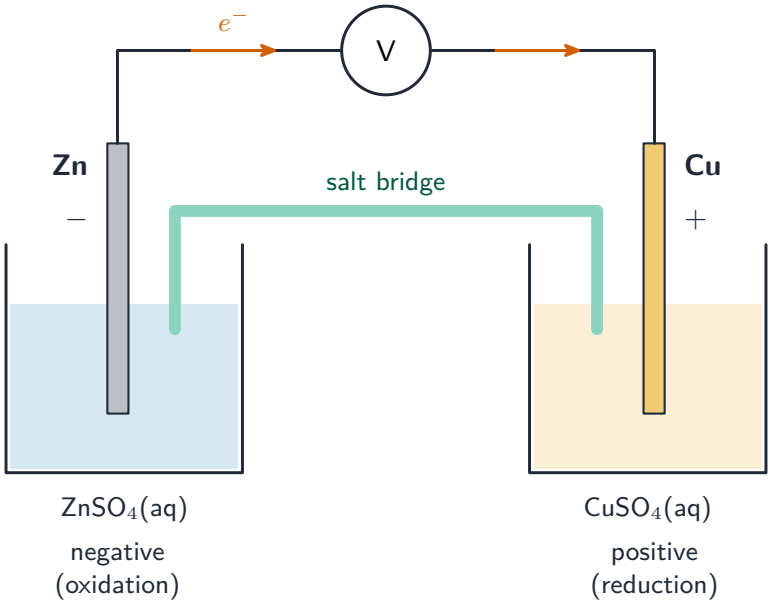
The standard hydrogen electrode: H_2 at 1 atm over platinum in 1 mol dm^{-3} H^+, the 0.00 V reference for every electrode potential

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:

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



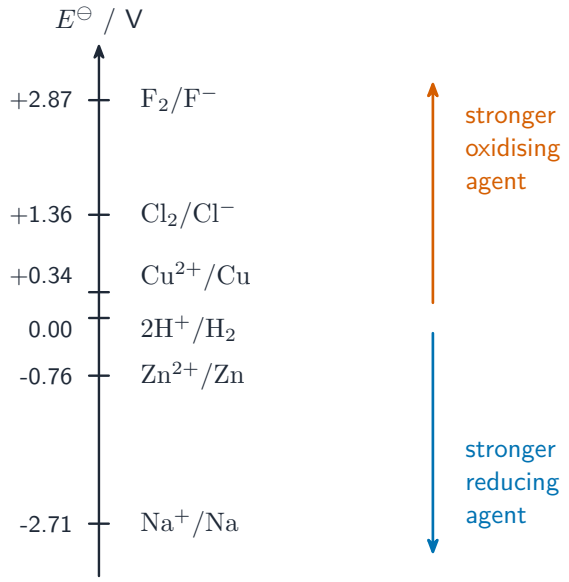
A simple cell: two half-cells joined by a salt bridge, with a voltmeter. Electrons flow from the negative (Zn) electrode to the positive (Cu)

Worked example. Find the standard cell potential of a cell built from the Zn^{2+}/Zn half-cell ($E^{\ominus} = -0.76$ V) and the Cu^{2+}/Cu half-cell ($E^{\ominus} = +0.34$ V).

$$E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{more positive}) - E^{\ominus}(\text{less positive}) = (+0.34) - (-0.76) = 1.10 \text{ V}.$$

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.

Exam tips

- $E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{more positive}) - E^{\ominus}(\text{less positive})$; a **positive** $E^{\ominus}_{\text{cell}}$ means the reaction is feasible.
- Standard conditions for $E^{\ominus}$: **298 K,** 1 **mol dm^{-3}, 100 kPa**, platinum electrode — state them if asked.
- A **more negative** electrode potential means a **stronger reducing agent**; use the series to predict the direction.
- For electrolysis quantities use $Q = It$ and moles of electrons $= Q/F$.