Redox equilibria

Standard electrode potentials and the hydrogen electrode, cell diagrams and emf, predicting feasibility and its limits, redox titrations, and fuel cells.

Electrode potentials

When a metal is placed in a solution of its ions, an equilibrium is set up:

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

The tendency of the species to gain electrons gives an **electrode potential**. It cannot be measured alone, so it is compared with a **reference electrode**: the **standard hydrogen electrode (SHE)**, defined as having $E^\ominus = 0.00$ V.

The **standard electrode potential**, $E^\ominus$, is the emf of a half-cell connected to the standard hydrogen electrode, measured under **standard conditions**:

- temperature **298 K**,
- pressure of **100 kPa** for any gases,
- **1.00 mol dm^{-3}** concentration of all ions in the half-cells.

The standard hydrogen electrode

- A platinum electrode (covered in finely divided platinum black, which acts as a catalyst) in contact with **hydrogen gas at 100 kPa**,
- immersed in a solution of **1.00 mol dm^{-3}** H^+ (e.g. HCl),
- at 298 K.

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \qquad E^\ominus = 0.00 \text{ V}$$

Other half-cells

- **A metal in contact with its ions**: the metal strip is the electrode.
- **Ions of the same element in different oxidation states** (such as Fe^{3+}/Fe^{2+} or MnO_4^-/Mn^{2+}): an **inert platinum electrode** dips into a solution containing both ions at 1.00 mol dm^{-3}.
- **A non-metal and its ions** (such as Cl_2/Cl^-): platinum electrode with gas bubbled over it.

The cells are connected by a **salt bridge** (filter paper soaked in KNO_3 solution) which completes the circuit with ion movement but does not allow the solutions to mix. A **high-resistance voltmeter** measures the emf with almost no current flowing.

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Electrochemical series

Standard electrode potentials are written as **reduction potentials**: the species on the left gains electrons. A list in order is the **electrochemical series**.

Half-equation	$E^\ominus$ / V
$Li^+ + e^- \rightleftharpoons Li$	−3.04
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.44
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.51

The more positive $E^\ominus$ is, the greater the tendency to be reduced, so the stronger an oxidising agent the species on the left is. The more negative it is, the stronger the reducing agent the species on the right.

Cell emf and diagrams

$$E^\ominus_{cell} = E^\ominus_{\text{positive electrode}} - E^\ominus_{\text{negative electrode}} = E^\ominus_{\text{right}} - E^\ominus_{\text{left}}$$

The more positive half-cell is the positive electrode and is where **reduction** occurs.

Conventional cell diagram: the half-cell with the **more negative** potential on the left (oxidation, anode), the more positive on the right, with a single vertical line for each phase boundary and a double line (or dashed) for the salt bridge:

$$Zn(s)\,|\,Zn^{2+}(aq)\,\|\,Cu^{2+}(aq)\,|\,Cu(s) \qquad E^\ominus_{cell} = +0.34 - (-0.76) = +1.10\ \text{V}$$

For half-cells with a platinum electrode, show both ions: $Pt\,|\,Fe^{2+}(aq),\ Fe^{3+}(aq)$.

TRY IT

Calculate $E^\ominus_{cell}$ for the cell with Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu half-cells, and write the cell reaction.

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$E^{\ominus}_{cell} = +0.77 - (+0.34) = +0.43$ V. The iron half-cell is positive, so Fe^{3+} is reduced and copper is oxidised: $2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+}$.

Core Practical 12 builds cells from metals and their ions, and measures the emf values.

Predicting feasibility

A reaction is **thermodynamically feasible** if $E^{\ominus}_{cell} > 0$.

The relationship with other quantities (given as a proportion):

$E^{\ominus}_{cell} \propto \Delta S_{total}$ $\quad$ $E^{\ominus}_{cell} \propto \ln K$

A positive $E^{\ominus}_{cell}$ means a positive ΔS_{total} and $K > 1$.

Disproportionation

To test whether a species disproportionates, compare the two half-equations in which it is reduced and oxidised. If $E^{\ominus}$ for the reduction of the species is **more positive** than that for the oxidation of the species (the overall $E^{\ominus}_{cell} > 0$), then disproportionation is feasible. For example, copper(I) disproportionates in aqueous solution: $2Cu^{+} \rightarrow Cu^{2+} + Cu$, with $E^{\ominus}_{cell} = +0.52 - 0.15 = +0.37$ V.

Limitations

Feasibility predictions from $E^{\ominus}$ values may not be correct because:

- the reaction may be **kinetically slow** (high activation energy), even if feasible,
- **conditions may not be standard** (different concentration, temperature or pressure change E).

Redox titrations

Iron(II) and manganate(VII)

$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

- Potassium manganate(VII) (purple) in the **burette**; the end point is the first permanent **pale pink** colour. It is its own indicator, since Mn^{2+} is almost colourless.
- Acidify with **dilute sulfuric acid** (not HCl, since MnO_4^- oxidises chloride, and not nitric acid, which is itself an oxidising agent).
- Read the burette at the top of the meniscus because the solution is deeply coloured.

> **TRY IT**

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25.0 cm^3 of an iron(II) solution needs 22.5 cm^3 of 0.0200 mol dm^{-3} $KMnO_4$. Find the concentration of Fe^{2+}.

$n(MnO_4^-) = 0.0200 \times 0.0225 = 4.50 \times 10^{-4}$ mol. Ratio 1 : 5, so $n(Fe^{2+}) = 2.25 \times 10^{-3}$ mol. $c = 2.25 \times 10^{-3}/0.0250 = 0.0900$ mol dm^{-3}.

Iodine and thiosulfate

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

Used to find the amount of an oxidising agent, which first oxidises excess iodide to iodine ($2I^- \rightarrow I_2$). The iodine is titrated with **sodium thiosulfate**. The indicator is **starch**, added **near the end point** when the iodine colour has faded to pale yellow. The blue-black colour disappears at the end point.

Examples: the percentage of copper in brass ($2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$), or the concentration of bleach.

Core Practicals 13a and 13b use both titrations.

Fuel cells

A **fuel cell** converts the energy of the reaction of a fuel with oxygen into a voltage, continuously, as long as the fuel is supplied. Fuels include hydrogen and hydrogen-rich fuels such as methanol.

	Acidic electrolyte	Alkaline electrolyte
Negative electrode (anode, oxidation)	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
Positive electrode (cathode, reduction)	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

The overall reaction is $2H_2 + O_2 \rightarrow 2H_2O$ in both. The only product is water.

NOTE

Advantages of fuel cells: no pollution at the point of use, and higher efficiency than burning fuels. Disadvantages: hydrogen is flammable and difficult to store, and its production needs energy.

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