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Chemistry

For the IB Diploma

Brighter Thinking
Better Learning

Chapter 20

Electron transfer reactions

Redox

Oxidation and reduction always occur together.

Oxidation	loss of hydrogen	gain of oxygen
Reduction	gain of hydrogen	loss of oxygen

Oxidation: loss of electrons or increase in oxidation state.

Reduction: gain of electrons or decrease in oxidation state.

Oxidising and reducing agents

Oxidising agent (oxidant) oxidises other species and, in the process, is itself reduced; an oxidising agent takes electrons away from another species.
Cu^{2+} is the oxidising agent in the reaction shown.

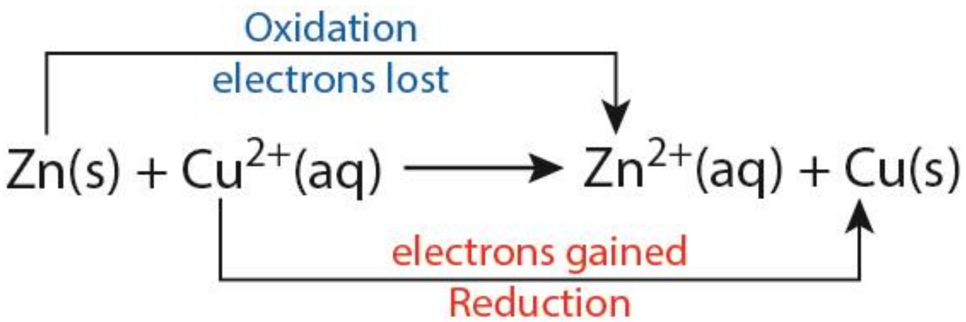


Figure 20.1: Oxidising and reducing agents.

Reducing agent (reductant) reduces other species and, in the process, is itself oxidised; a reducing agent gives electrons to another species.
Zn is the reducing agent in the reaction shown.

Using oxidation states to identify species oxidised and reduced

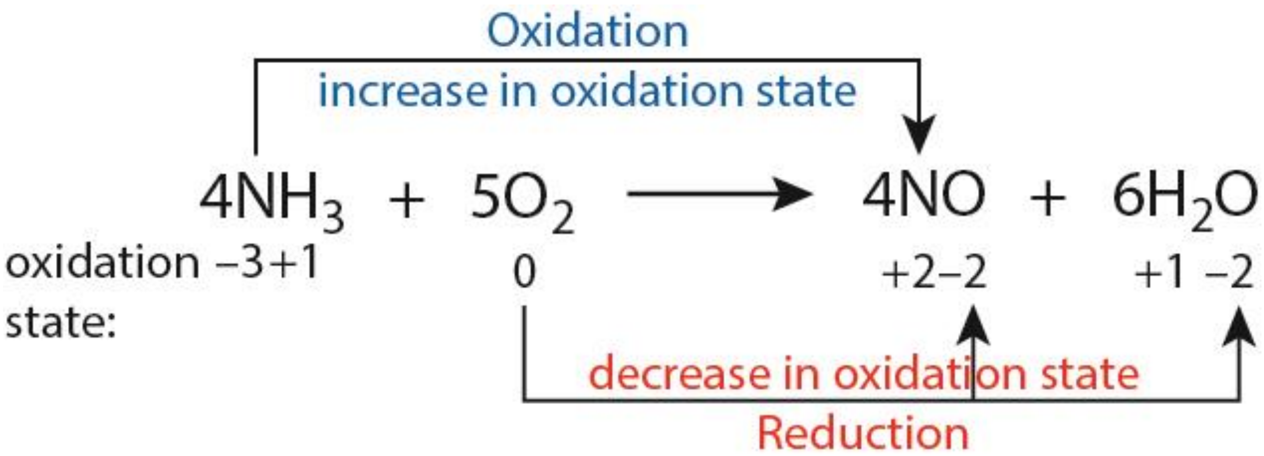


Figure 20.2: Using oxidation states to identify species being oxidised and reduced.

Half-equations

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$	reduction
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$	oxidation

Deducing half-equations in acidic solution

$IO_3^- \rightarrow I_2$

1 Balance all atoms except H and O.

2 Add H_2O to the side deficient in O to balance O.

3 Add H^+ to the side deficient in H to balance H.

4 Add e^- to the side deficient in negative charge to balance charge.

$12H^+ + 2IO_3^- + 10e^- \rightarrow I_2 + 6H_2O$

Balancing redox equations in acidic solution using the half-equation method

$Cr_2O_7^{2-}(aq) + Cl^-(aq) \rightarrow Cr^{3+}(aq) + Cl_2(g)$

$As_2O_3(s) + NO_3^-(aq) \rightarrow H_3AsO_4(aq) + NO(g)$

Work out the answers.

Redox titrations

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

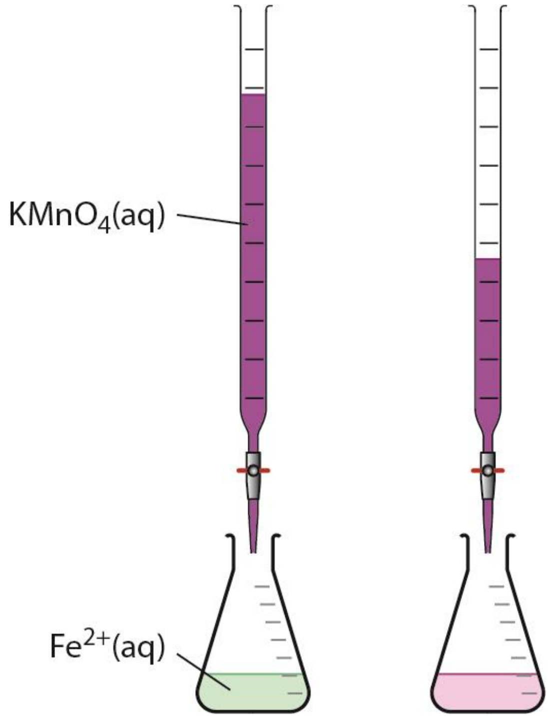


Figure 20.3: Redox titrations.

This reaction does not need a separate indicator, it is self-indicating.

A displacement reaction

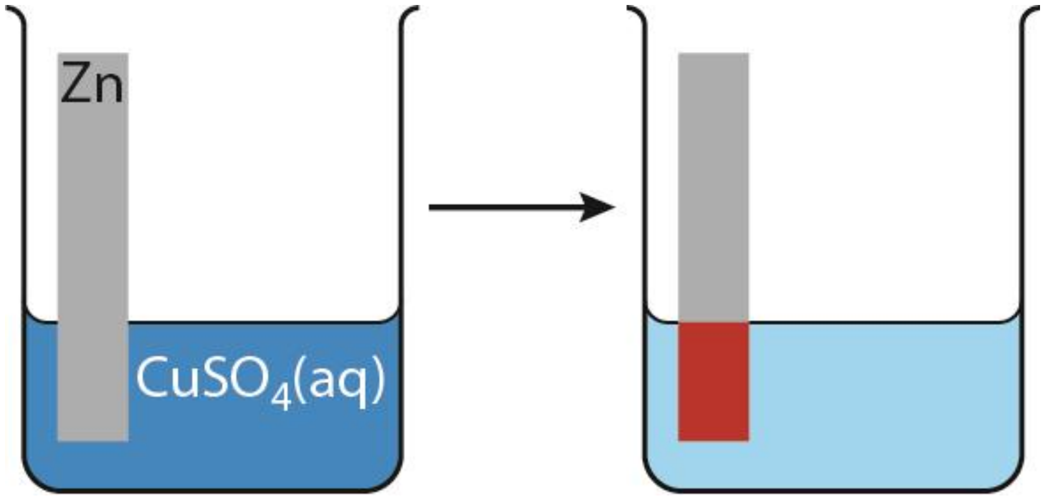


Figure 20.4: Zinc displaces copper ions from solution.

Zinc is higher up in the activity series than copper. This means zinc is more readily oxidised than copper (more reactive than copper) and, therefore, displaces copper ions from solution

Voltaic cells

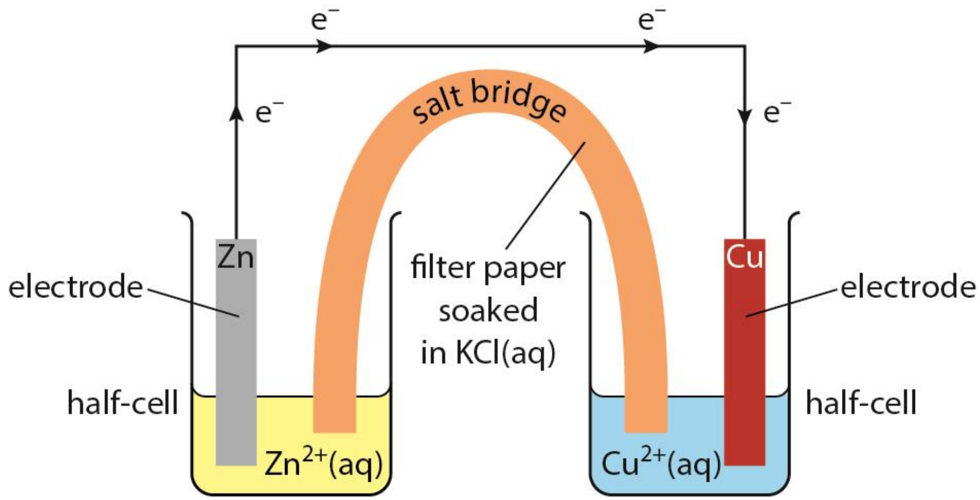


Figure 20.5: A voltaic cell.

Anode: the electrode at which oxidation occurs.

Cathode: the electrode at which reduction occurs.

Salt bridge: completes the circuit in a voltaic cell by providing an electrical connection between two half-cells, allowing ions to flow into or out of the half-cells to balance out the charges in the half-cells. A salt bridge contains a concentrated solution of an ionic salt, such as KCl.

Electromotive force: a standard cell potential produced when two half-cells are connected under standard conditions.

Nickel–cadmium battery – secondary cells

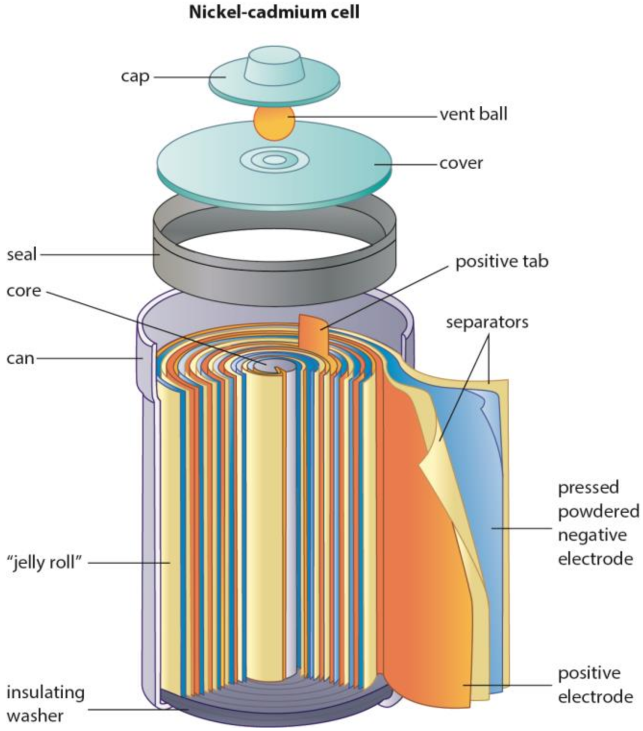


Figure 20.6: Illustration of a nickel–cadmium cell.

Figure 20.7: Examples of secondary cells.

Anode: $Ni(OH)_2(s) + OH^-(aq) \rightarrow NiO(OH)(s) + H_2O(l) + e^-$

Cathode: $Cd(OH)_2(s) + 2e^- \rightarrow Cd(s) + 2OH^-(aq)$

Overall: $Cd(OH)_2(s) + 2Ni(OH)_2(s) \rightarrow Cd(s) + 2NiO(OH)(s) + 2H_2O(l)$

Electrolytic cells

Comparison between electrolytic and voltaic cells

Electrode	Electrolytic cell	Voltaic cell
Anode	Positive	Negative
Cathode	Negative	Positive

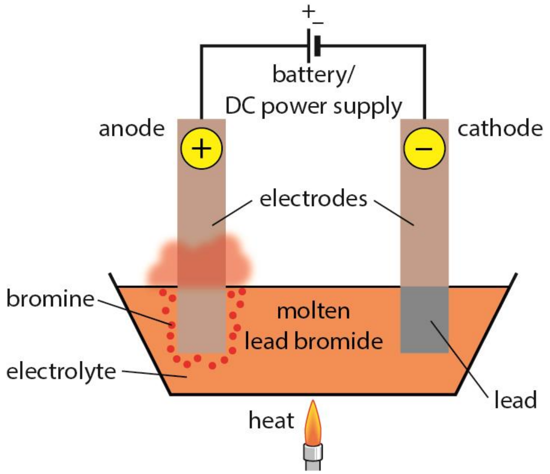


Figure 20.8: An electrolytic cell.

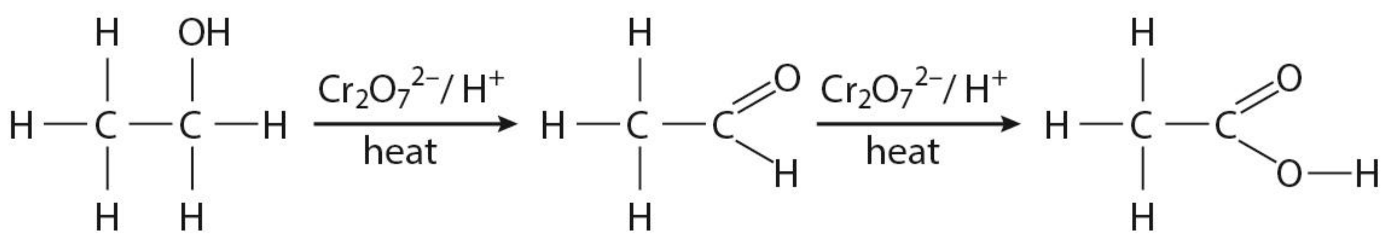
Electrolyte: a solution, or a molten compound, that will conduct electricity due to the presence of ions that are free to move towards the electrodes.

Reactions of alcohols

Primary alcohols

$$\text{primary alcohol} \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+} \text{aldehyde} \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+} \text{carboxylic acid}$$

e.g.



ethanol ethanal ethanoic acid

Oxidation

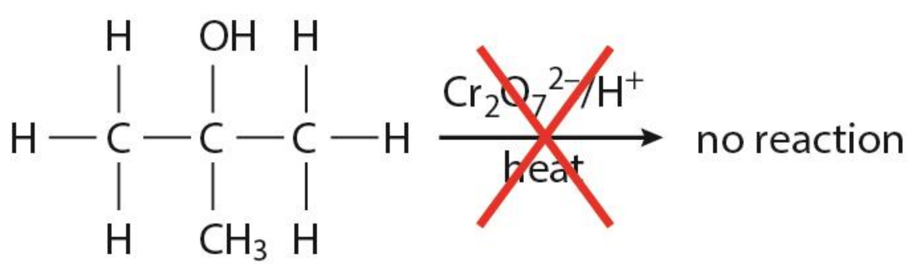
Secondary alcohols

secondary alcohol $\xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+}$ ketone $\cancel{\xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+}}$

e.g.

propan-2-ol propanone

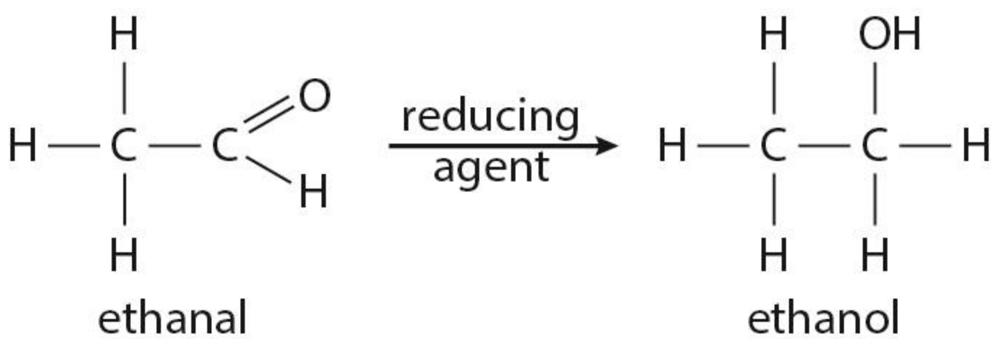
Tertiary alcohols

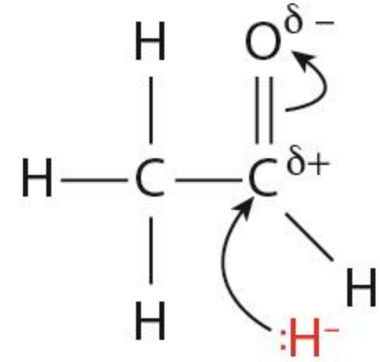


2-methylpropan-2-ol

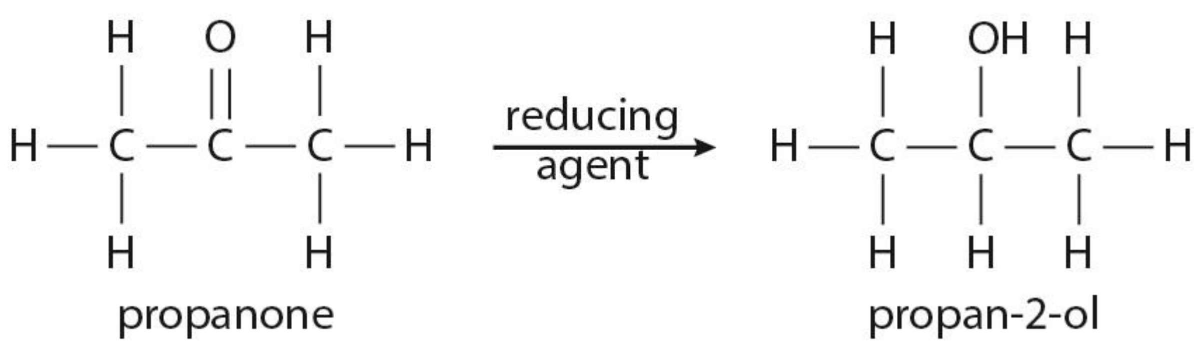
Reduction reactions

Aldehydes are reduced to primary alcohols, e.g.



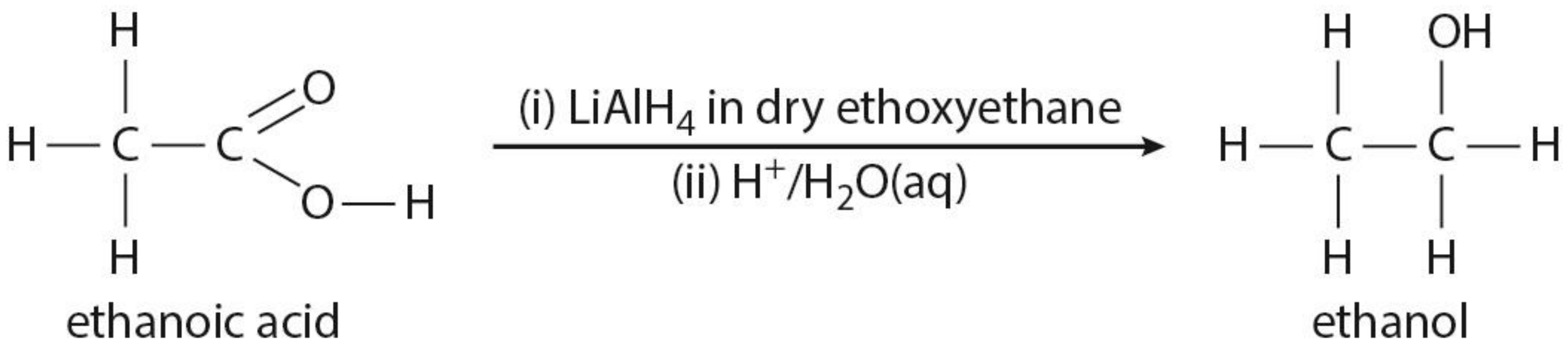


Ketones are reduced to secondary alcohols, e.g.



Reduction reactions

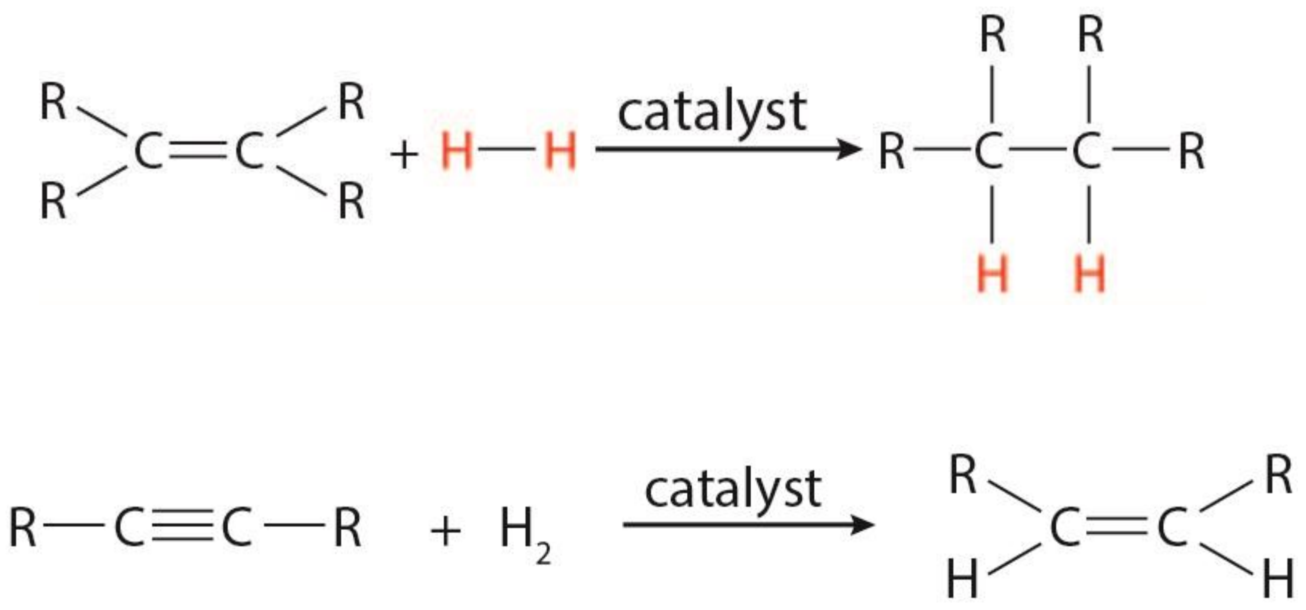
Carboxylic acids are reduced to primary alcohols, e.g.



The reduction cannot be stopped at the aldehyde stage.

Reduction reactions

Alkenes and alkynes can be reduced by adding H_2 in the presence of a catalyst.



Standard hydrogen electrode

Standard cell potential: the electromotive force (voltage) produced when two half-cells are connected under standard conditions (all concentrations 1 mol dm^{-3} and pressure 100 kPa). This drives the movement of electrons through the external circuit from the negative electrode to the positive electrode.

$$E^\ominus$$

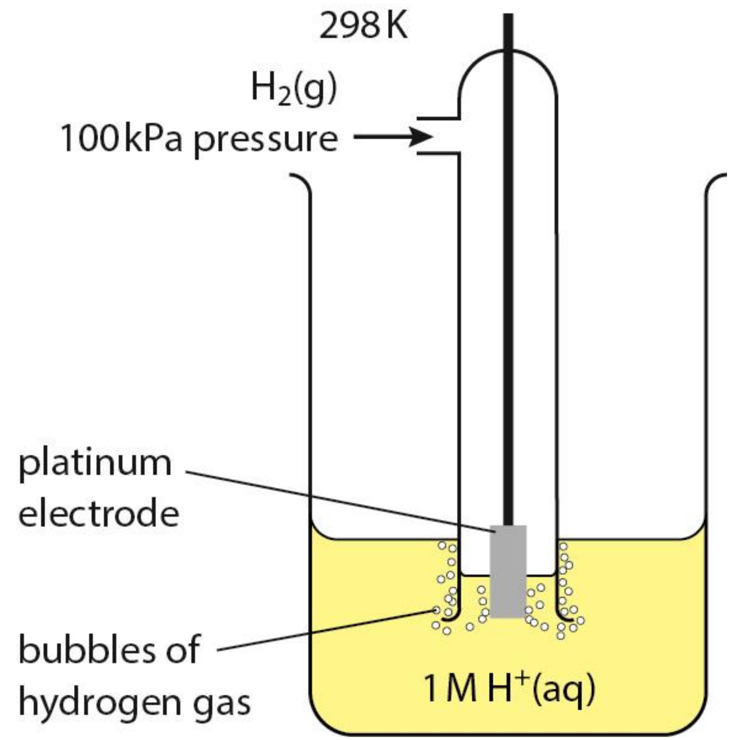


Figure 20.9: The standard hydrogen electrode.

Measuring standard electrode potentials

The more negative the standard electrode potential, the stronger the reducing agent.

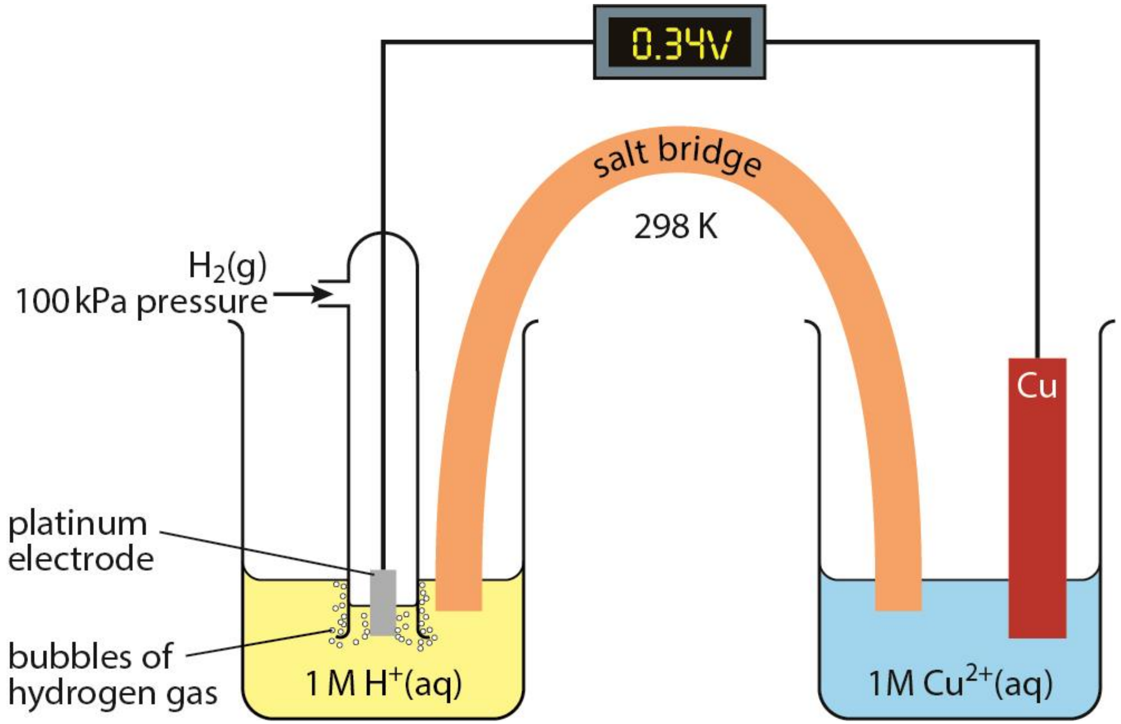


Figure 20.10: Measuring the standard electrode potential of the Cu^{2+}/Cu half-cell.

Calculating standard cell potentials

1. Write down the half-equations and standard electrode potentials for the two reactions involved.
2. Change the sign of the more negative (less positive) standard electrode potential and add it to the other electrode potential.

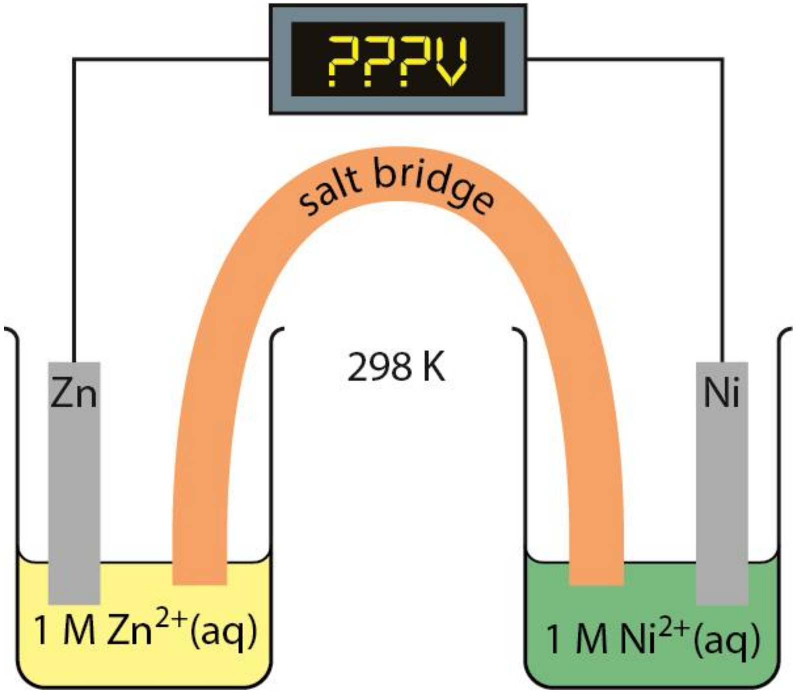
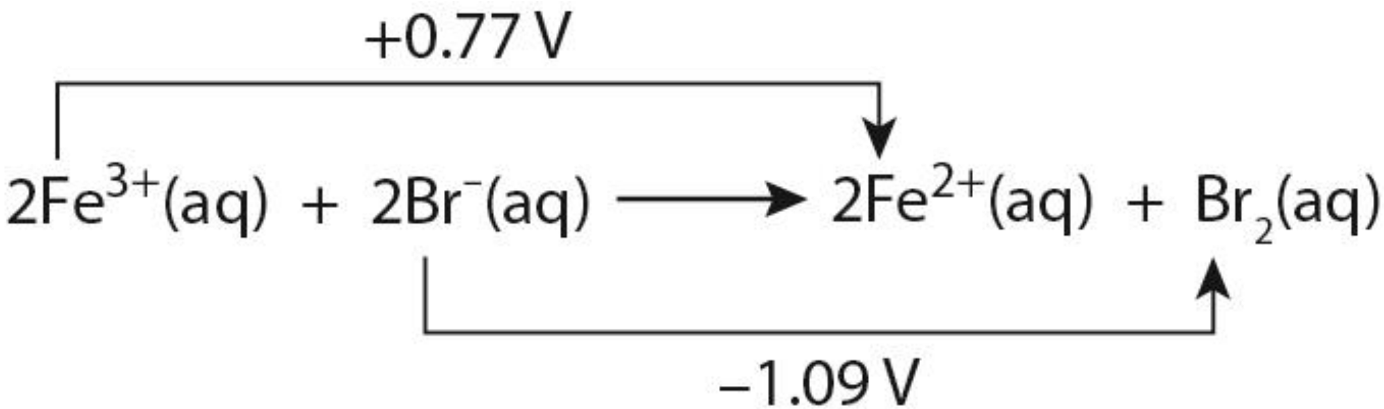


Figure 20.11: A zinc–nickel cell.

Using standard electrode potentials to predict the feasibility of a redox reaction



The overall cell potential will be negative (–0.32 V), so the reaction will not be spontaneous and Br^- will not reduce iron(III) to iron(II).

Standard cell potentials and $\Delta G^{\ominus}$

$\Delta G^{\ominus} = {}^{-}nFE^{\ominus}$

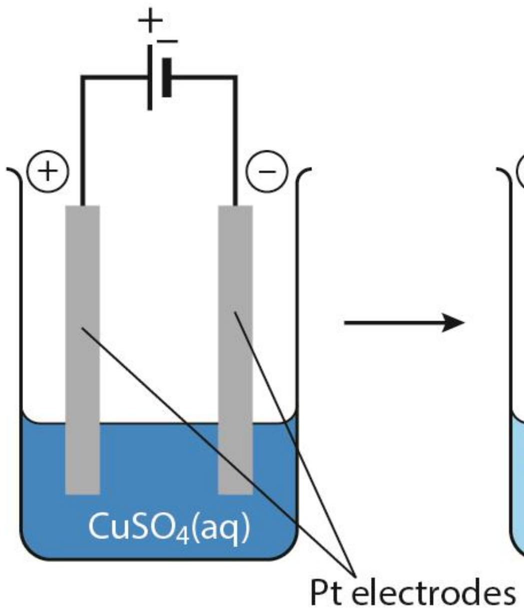
n is the number of electrons transferred in a redox reaction

F is the Faraday constant, which is equal to the charge on one mole of electrons and has a value of approximately 96 500 C mol^{-1}.

The units of $\Delta G^{\ominus}$ in this equation are J mol^{-1}.

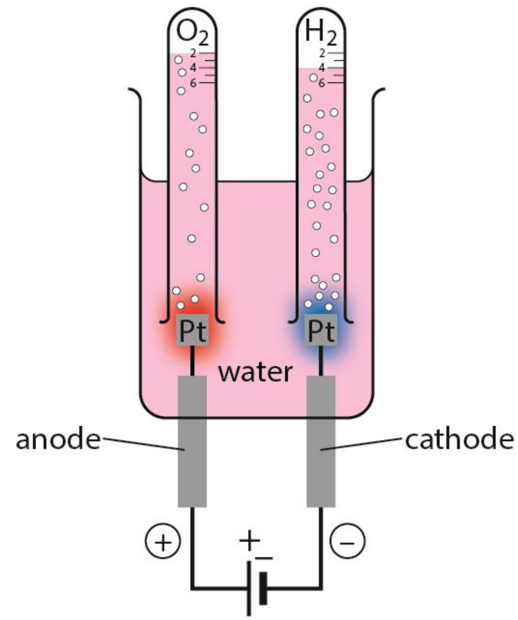
$E^{\ominus}_{cell}$	$\Delta G^{\ominus}$	Is the reaction spontaneous?
Positive	Negative	Yes
Negative	Positive	No

Electrolysis of aqueous solutions



$CuSO_4$ (aq) with inert electrodes

Figure 20.12: Electrolysis of copper(II) sulfate solution using platinum electrodes.



Acidified water

Figure 20.13: Electrolysis of acidified water to which some universal indicator has been added.

Electroplating

Electroplating: the process of coating an object with a thin layer of a metal using electrolysis.

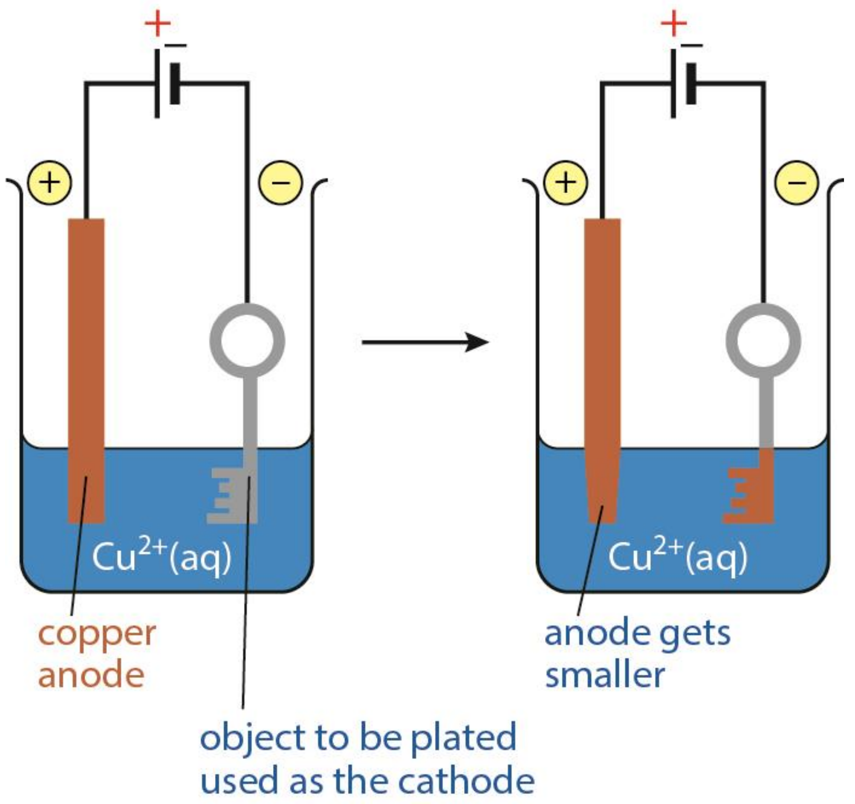


Figure 20.14: Experimental set-up for electroplating a key with copper.