3.1 Standard electrode potential

Zinc metal is placed into an aqueous solution of copper(II) sulfate. The blue colour of the solution fades and a reddish deposit is seen on the zinc.

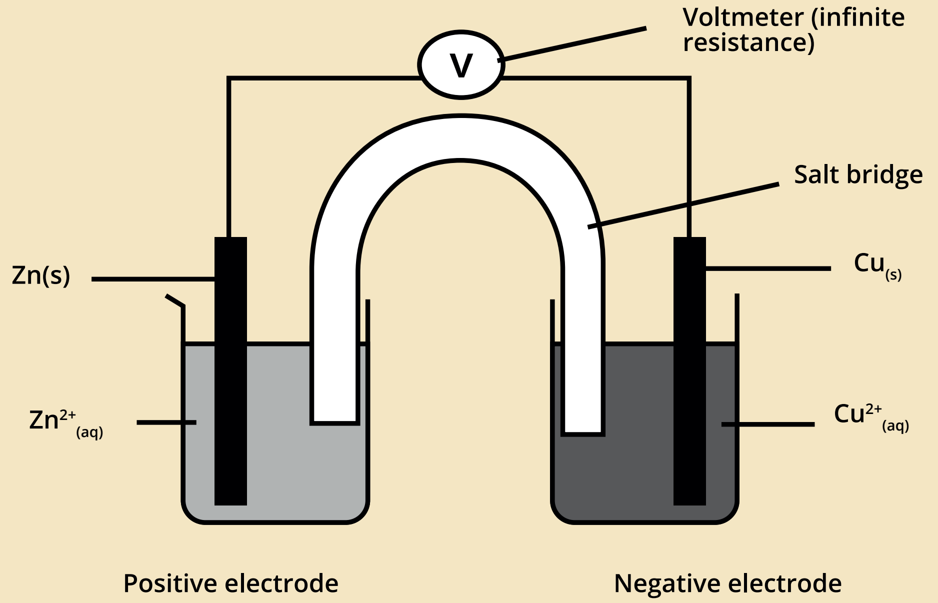
A redox reaction has taken place.

$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$ and $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$

Overall reaction

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

$Zn^{2+}(aq)$ is colourless so the blue colour of the aqueous $Cu^{2+}(aq)$ disappears. If the two halves of the reaction are kept separate, chemical energy is changed into electrical energy producing a voltage.



The salt bridge allows ions to flow from one solution to the other while the two solutions are kept separate. The salt bridge is filter paper that is soaked in potassium nitrate solution. All potassium salts and all nitrates are soluble so no precipitate can form in the salt bridge stopping the flow of ions.

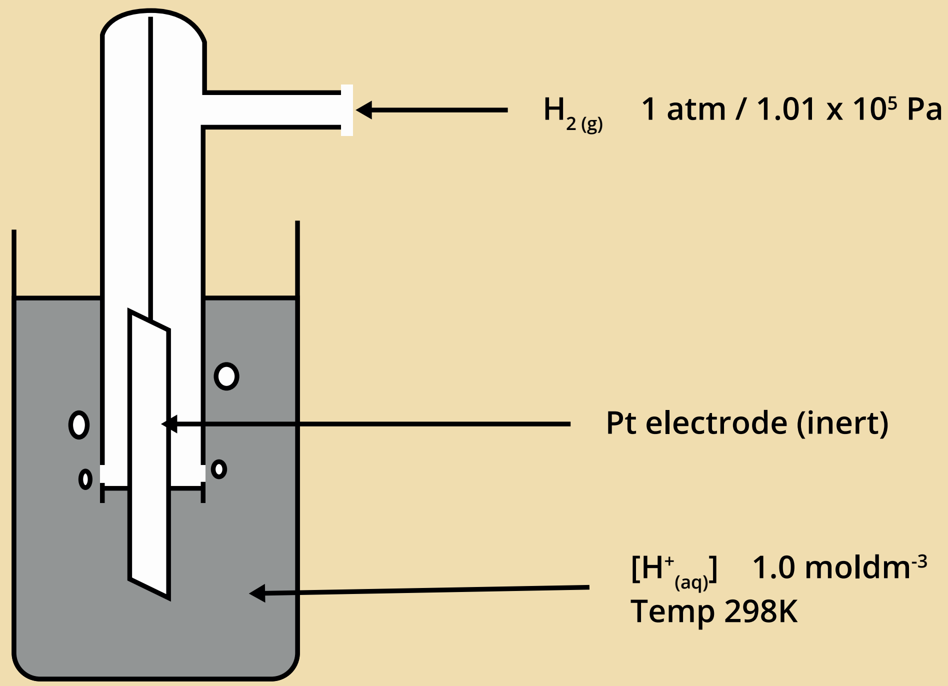
Electrons are released at the negative zinc electrode and flow through the external wire to the positive copper electrode where copper ions accept electrons. This can only happen if the voltmeter is short-circuited, as electrons cannot flow through the voltmeter due to its high resistance.

Cell diagrams

The dotted line is the salt bridge and the solid line shows a change of state. The positive electrode is written on the right-hand side.

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \; \vdots\vdots \; Cu^{2+}_{(aq)} \mid Cu_{(s)}$$

Combining two electrodes produces an EMF (voltmeter reading). By convention all such emfs are measured with respect to the standard hydrogen electrode (SHE).



By convention the electrode process at the platinum electrode is taken as the standard and other potentials are measured with respect to it.

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

The standard electrode potential, E^θ, of a half cell, $Zn^{2+}(aq)/ Zn(s)$, is the EMF represented by the cell diagram

$$Pt(s)|H_2(g)|2H^+(aq) \; \vdots\vdots \; Zn^{2+}(aq)|Zn(s)$$

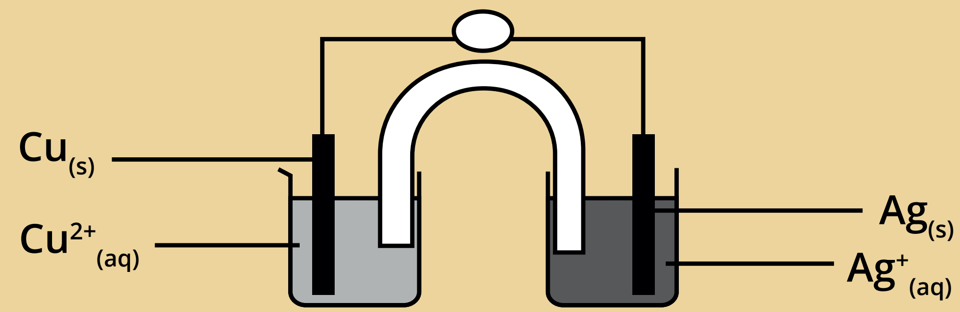
Standard conditions

298K / 1.0 mol dm^{-3} / 1 atm

The sign of E^θ is the sign of the right-hand electrode in the cell diagram. The emf is the potential difference across the cell and is a measure of the maximum amount of energy which can be given by the cell.

Calculating the EMF of a cell

Consider the following practical setup.



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

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $\quad E^\theta = +0.80$ V

The reaction with the more positive E^θ will proceed in the forward direction (to the right).

The overall reactions are

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

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $\quad E^\theta = +0.80$ V

EMF = +0.80 – 0.34 = +0.46V

(positive EMF of the system means feasible reaction)

Fuel cells

H_2 is fed into the anode on one side of the cell while O_2 from the air is fed to the cathode on the other side. Under the influence of the Pt catalyst, the H_2 is ionised.

$$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$$

At the cathode O_2, H^+ and electrons form the waste product of the device which is water.

$$\tfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O(l)$$

Advantages - clean technology, high efficiency, quiet operation and relatively simple construction.
Disadvantages - expensive, storage of hydrogen poses problems as hydrogen is a very flammable and explosive gas and present cells last for a much shorter time than necessary to be economically viable.