Redox equilibria

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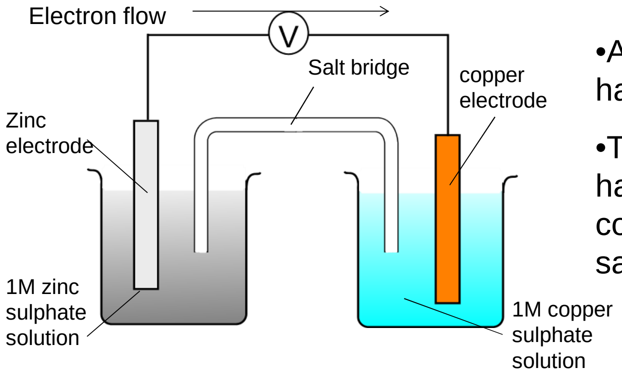
Main features of an electrochemical cell

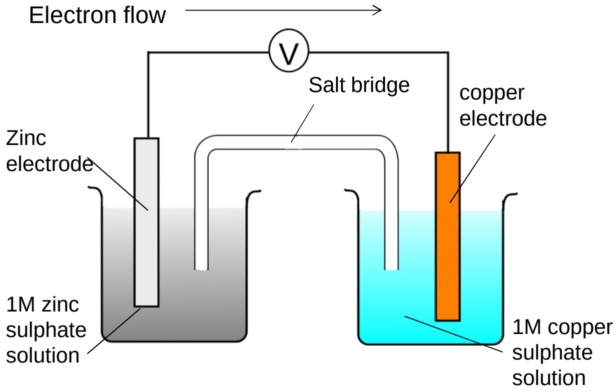


- A cell will have two half–cells.
- The two half cells have to be connected with a salt bridge.

- Generally a half cell will consist of a metal and a solution of that metal (eg Cu and $CuSO_{4)}$.

These two electrodes which will produce a small voltage if connected into a circuit. (i.e. become a Battery or cell).

Completing the circuit with a Salt Bridge



•A salt bridge is usually made from a piece of filter paper (or material) soaked in a salt solution, usually Potassium Nitrate. The salt bridge is used to connect up the circuit.
•A wire is not used because the metal wire would set up its own electrode system with the solutions.

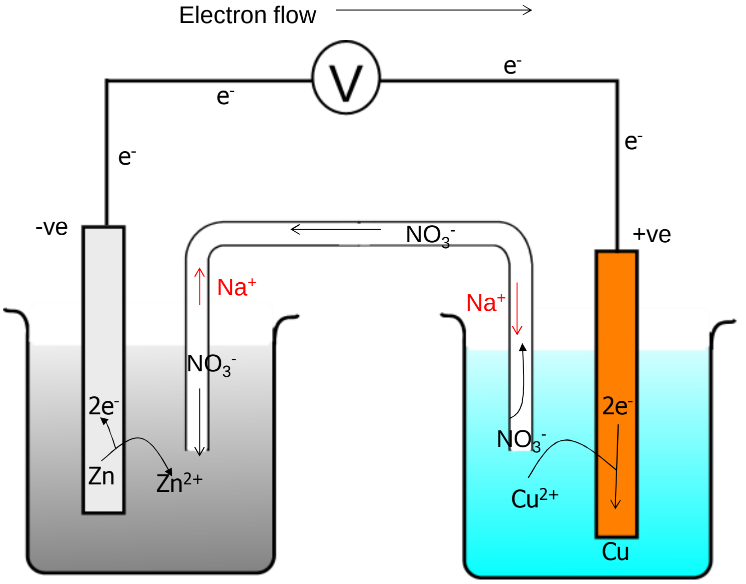
Why does a voltage form?

- When connected together the zinc half-cell has more of a tendency to oxidise to the Zn^{2+} ion and release electrons than the copper cell.
- More electrons will therefore build up on the zinc electrode than the copper electrode.
- So there is a potential difference between the two electrodes.
- The zinc strip is the negative terminal and the copper strip is the positive terminal.

This potential difference is measured with a high resistance voltmeter, and is given the symbol E.

The E for the Daniell cell is E= +1.1V.

Electron flow in cell



$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ $\quad$ $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

High Resistance Voltmeters

The voltmeter needs to be of very high resistance to stop the current from flowing in the circuit. In this state it is possible to measure the maximum possible potential difference (E).

The reactions will not be occurring because the very high resistance voltmeter stops the current from flowing.

However, if the voltmeter is removed and replaced with e.g. a bulb or if the circuit is short circuited, a current flows. The reactions will then occur separately at each electrode.

•The most positive electrode will always undergo reduction.

•The most negative electrode will always undergo oxidation.

The chemical reactions occur

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

Cell Diagrams

Electrochemical cells can be represented by a cell diagram:

$Zn(s) \mid Zn^{2+}(aq) \,\vdots\vdots\, Cu^{2+}(aq) \mid Cu(s)$ E= +1.1V

- solid vertical line represents the phase boundary usually between solid (electrode) and solution (electrolyte)
- Double line (central) represents salt bridge division between the two half cells
- the voltage produced is indicated
- positive half cell is written on the right if possible (but this is not essential)

If a half equation has several physical states then the solid vertical line should be used between each different state boundary

$4e^- + 2H_2O(l) + O_2(g) \rightarrow 4OH^-(aq) \longrightarrow \,||\, O_2 \mid H_2O, OH^- \mid Pt$

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $||\, Cl_2 \mid 2Cl^- \mid Pt$

As the phase line also separates the oxidised and reduced terms a comma is not necessary here

Systems that do not include metals.

If a system does not include a metal, then a platinum electrode must be used and included in the cell diagram.

e.g. Fe^{2+} (aq) → Fe^{3+} (aq) + e^- .

The cell diagram is drawn as:

¦ Fe^{3+} (aq), Fe^{2+}(aq) |Pt

Still with more oxidised on left

A comma separates the oxidised from the reduced species

If the system contains several species

e.g. MnO_4^- + $8H^+$ + $5e^-$ → Mn^{2+} + $4H_2O$

then you don't have to include the H^+, H_2O

¦ MnO_4^-, Mn^{2+} |Pt

Calculating the EMF of a cell

Mg(s)| Mg^{2+}(aq) ¦¦ Cu^{2+} (aq) | Cu (s)

Each half cell has a standard value
Mg^{2+} (aq)| Mg(s) E= -2.37V
Cu^{2+} (aq) | Cu (s) E = +0.34V

Use the equation $E_{cell} = E_{rhs} - E_{lhs}$

$E_{cell} = 0.34 - -2.37$

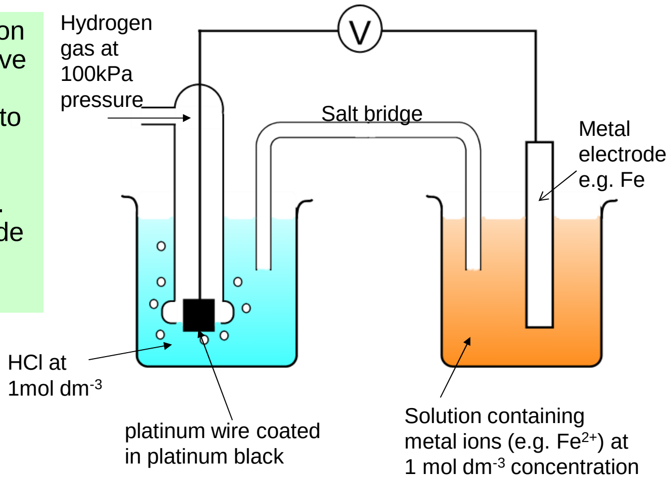
The E cell = + 2.71 V

If one requires the cell to be positive then the most positive electrode is placed on the right hand side.

The hydrogen electrode

It is not possible to measure the absolute potential of a half electrode on its own. It is only possible to measure the potential difference between two electrodes.

However, by convention we can assign a relative potential to each electrode by linking it to a reference electrode, which is given a potential of zero Volts. The hydrogen electrode is the reference electrode



The hydrogen electrode equilibrium is:

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

Because the equilibrium does not include a conducting metal surface a platinum wire is used which is coated in finely divided platinum. (The platinum black acts as a catalyst, because it is porous and can absorb the hydrogen gas.)

In a cell diagram the hydrogen electrode is represented by:

$Pt \mid H_2\,(g) \mid 2H^+\,(aq) \vdots$

To make the electrode a standard reference electrode some conditions apply:

1. Hydrogen gas at pressure of 100kPa
2. Solution containing the hydrogen ion at 1 M (solution is usualy 1M HCl)
3. Temperature at 298K

Secondary standards

- The Standard Hydrogen Electrode is difficult to use, so often a different standard is used which is easier to use.
- These other standards are themselves calibrated against the SHE.
- This is known as using a **secondary standard -** i.e. a standard electrode that has been calibrated against the primary standard.
- The common ones are:
- silver / silver chloride E = +0.22 V
- calomel electrode E = +0.27 V

Standard Electrode Potentials

When an electrode system is connected to the hydrogen electrode system, and standard conditions apply the potential difference measured is called the <u>standard electrode potential,</u> given the symbol $E^{\ominus}$.

The standard conditions are :
•ion solutions at 1M
•temperature 298K
•gases at 100kPa pressure

Standard electrode potentials are found in data books and are quoted as

$Li^{+}(aq) \mid Li (s)$ E= -3.03V

more Oxidised on left

They may also be quoted as half equations

$Li^{+}(aq) + e^{-} \rightleftharpoons Li (s)$ E= -3.03V

Using electrode potentials

The most useful application of electrode potentials is to show the direction of spontaneous change for redox reactions

The easiest way to use electrode potentials is as follows:

For any two half equations

The more **negative** half cell will always **oxidise** (go backwards)

Mg^{2+} (aq) + $2e^-$ → Mg(s) E= -2.37V

Cu^{2+} (aq) + $2e^-$ → Cu (s) E = +0.34V

The more **positive** half cell will always **reduce** (go forwards)

The reaction would be

Mg + Cu^{2+} → Cu + Mg^{2+}

+ve half cells will tend to attract electrons and so reduce

What reaction occurs when two half cells are put together?

Zn^{2+}(aq)| Zn(s) E= - 0.76V

Fe^{2+}(aq)| Fe(s) E= -0.44V

The more **positive** electrode will **reduce** with zinc and go from **left to right**

Fe^{2+}(aq) +$2e^-$ → Fe(s)

The most **negative** electrode will **oxidise** and go from **right to left**

The half equation is therefore Zn(s) → Zn^{2+}(aq) +$2e^-$

To get the full equation of the reaction add the two half reactions together, cancelling out the electrons.

Zn + Fe^{2+} → Fe + Zn^{2+}

Using series of standard electrode potentials

Most strong reducing agents found here

oxidation

As more **+ve** increasing tendency for species on left to **reduce,** and act as **oxidising agents**

Li^+ | Li	-3.03V
Mn^{2+}| Mn	-1.19V
$2H^+$ | H_2	0V
Ag^+ | Ag	+0.8V

As more **–ve** increasing tendency for species on right **to oxidise,** and act as **reducing agents**

Most strong oxidising agents found here

reduction

The most **powerful reducing agents** will be found at the most **negative** end of the series on the right (ie the one with the lower oxidation number)

The most **powerful oxidising agents** will be found at the most **positive** end of the series on the left (ie the one with the higher oxidation number)

Working out the direction of a redox reaction

Does this reaction occur?

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

Look up Standard electrode potentials

Zn^{2+}(aq)| Zn(s) E= - 0.76V oxidised

Cu^{2+} (aq) | Cu (s) E = +0.34V reduced

Decide which half-cell will be oxidised and which will be reduced

Use the following equation to work out Ecell

$E_{cell} = E_{reduced} - E_{oxidised}$

= 0.34 - -0.76

= + 1.10V

If the E_{cell} is positive the reaction will occur
If the E_{cell} is negative the reaction will not occur

In General

If the Ecell is positive the reaction will occur
If the Ecell is negative the reaction will not occur

However, values close to zero indicate an equilibrium.

- Ecell ≈ +0.1 indicates an equilibrium that favours products.
- Ecell ≈ -0.1 indicates an equilibrium that favours reactants.

Writing equations from cell diagrams

Problem: You are given a cell diagram and are asked to work out what reaction would occur if current was allowed fo flow.

$Ni (s) | Ni^{2+}(aq) || Fe^{3+} (aq), Fe^{2+}(aq) | Pt$

Fe^{3+} (aq), Fe^{2+}(aq) |Pt E= +0.77V

Ni^{2+}(aq) | Ni (s) E= -0.25V

Use the equation
$E_{cell} = E_{rhs} - E_{lhs}$

When E_{cell} is positive the reaction will go from left to right

$E_{cell} = 0.77 - -0.25$

The E cell = + 1.02 V

Therefore the reactants are Ni and Fe^{3+} and the products are $Ni^{2+} + Fe^{2+}$

To write a balanced equation turn the half–cells into half equations

$Ni \rightarrow Ni^{2+} + 2e^-$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ x 2

Combine to cancel out electrons

$Ni + 2Fe^{3+} \rightarrow Ni^{2+} + 2Fe^{2+}$

Summary of predicting if a reaction can occur

Ecell and equilibrium constants can all be used to predict if a reaction might occur.

Reaction 'does not go'	Reactants predominate in an equilibrium	equal amounts of products and reactants	Products predominate in an equilibrium	Reaction goes to completion
$K_c < 10^{-10}$	$K_c \approx 0.1$	$K_c = 1$	$K_c \approx 10$	$K_c > 10^{10}$
E < -0.6	E≈ -0.1 V	E =0	E≈ +0.1 V	E>0.6 V

Complicating factors

- If the E_{cell} or entropy is positive and indicates a reaction might occur, there is still a possibility, however, that the reaction will not occur or will occur so slowly that effectively it doesn't happen.
- If the reaction has a high activation energy the reaction will not occur.

Non Standard Conditions

The E_{cell} uses standard conditions. If the E_{cell} is negative than the reaction is said not to occur. However, a reaction may occur when a E cell is negative under non-standard conditions.
For example using concentrated acid instead of 1M or a higher temperature than 298K