

Electrode Potentials and Fuel Cells

Redox

In an oxidation-reduction reaction or redox reaction, electrons pass from the reducing agent to the oxidising agent.

Oxidation state (number)

This is similar to valency. It is the number of electrons involved in bonding.

Half-reaction

Redox reactions can be split into two half reactions. Eg for

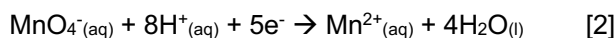
$\text{Cu}^{2+} + \text{Mg} \rightarrow \text{Mg}^{2+} + \text{Cu}$ This can be split into two half reactions which show electrons.

$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ and $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$ If you add these two equations together, you will obtain the full equation again as electrons cancel out.

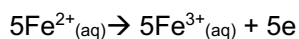
Oxidising agents - These are substances which can accept electrons from other substances, their oxidation number decreases.

Reducing agents - These are substances which can give electrons to other substances, their oxidation number increases.

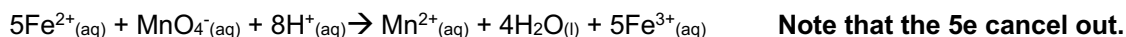
Constructing redox equations using half-equations



Equations must be balanced wrt mass and charge. These half equations are balanced wrt mass but not charge. Equation [1] only involves 1 e, equation [2] involves 5 e. Equation [1] must be multiplied by 5 to give:

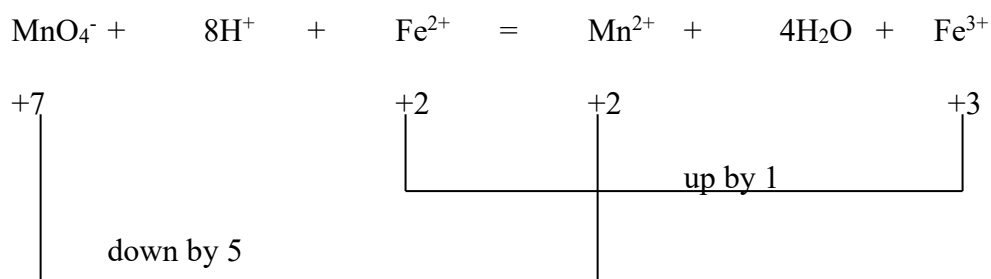


And then added to equation [2]

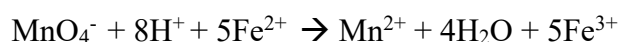


Constructing Redox Equations using oxidation numbers

1. Write the equation and balance it with respect to atoms.
2. Write oxidation numbers down of those that change so we can see clearly what has been oxidised and reduced.
3. Change in oxidation states must equal-if one atom goes up by two so the other must go down by 2.



Therefore in order to balance the oxidation numbers, iron must be multiplied by 5 to give:



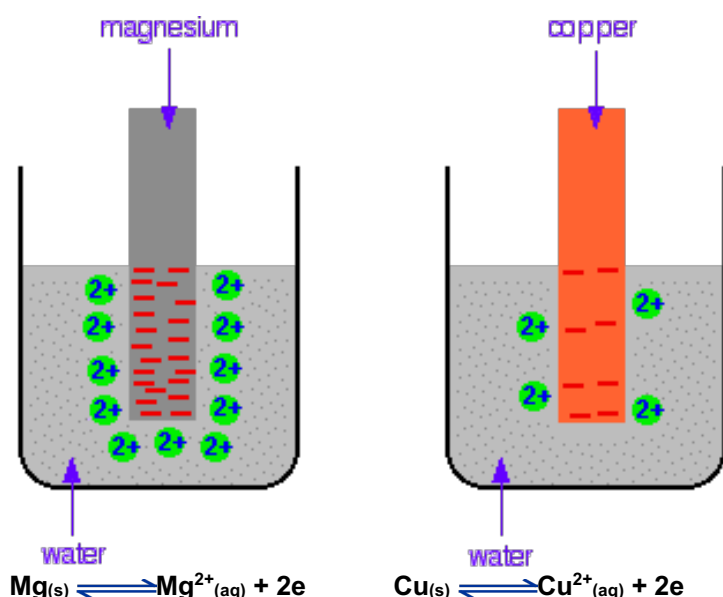
Electrode Potentials

Electrode potentials

A piece of metal in one of its salt solutions is a **half-cell (electrode)**.

For example: A piece of magnesium in a beaker of its ions.

There will be some tendency for the magnesium atoms to shed electrons and go into solution as magnesium ions. The electrons will be left behind on the magnesium. In a very short time, there will be a build-up of electrons on the magnesium, and it will be surrounded in the solution by a layer of positive ions. These will tend to stay close because they are attracted to the negative charge on the piece of metal. Some of them will be attracted enough that they will reclaim their electrons and stick back on to the piece of metal. A dynamic equilibrium will be established when the rate at which ions are leaving the surface is exactly equal to the rate at which they are joining it again. At that point there will be a constant negative charge on the magnesium, and a constant number of magnesium ions present in the solution around it.



Copper is less reactive than magnesium and so forms its ions less readily. Any ions which do break away are more likely to reclaim their electrons and stick back on to the metal again. You will still reach an equilibrium position, but there will be less charge on the metal, and fewer ions in solution.

A combination of two half-cells is an **(electrochemical) cell**.

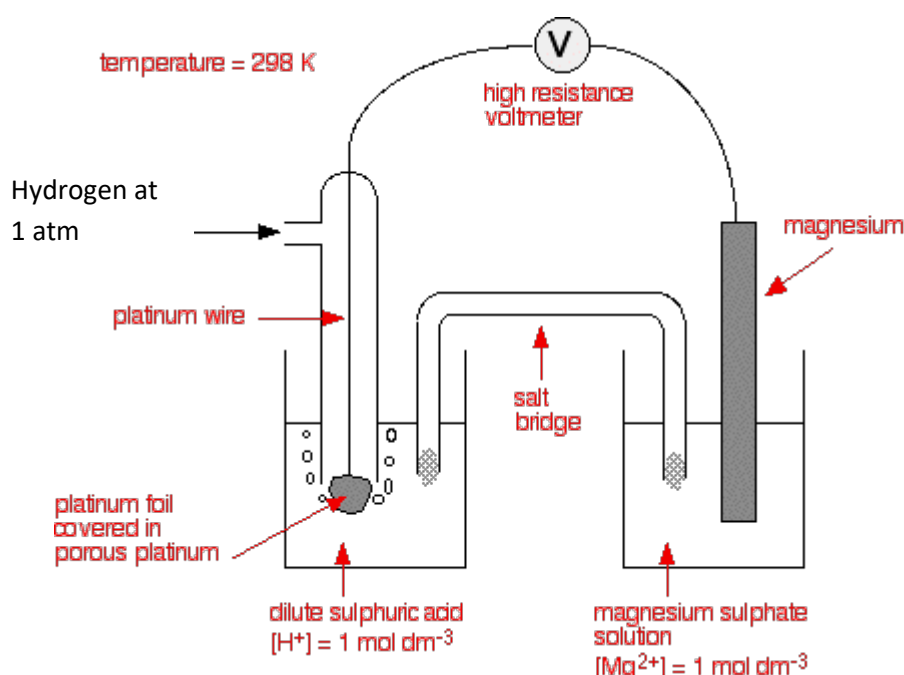
The standard electrode (redox) potential, E^\ominus , of a half-cell is the voltage produced when the electrode is connected to a standard hydrogen electrode. Standard conditions are: 298K, 1.00M aqueous solution, 1atm pressure.

Measurement of standard electrode potentials

Metals or non-metals in contact with their aqueous ions

A strip of pure metal is placed in a 1.00M aq soln of one of its ions and connected to a **standard hydrogen electrode** via a **salt bridge**. This is a strip of filter paper soaked in aq potassium nitrate which completes the electric circuit by allowing movement of ions between the two half-cells. (Electrons flow through the wire).

The standard hydrogen electrode is the standard reference electrode, E^\ominus taken as 0.00V.



For non-metals a half-cell consists of a platinum wire in contact with the element and its aqueous ions, e.g. chlorine gas and chloride ions. Platinum is used because it is an inert metal.

For ions of the same element in different oxidation states a half-cell consists of a piece of platinum in a solution containing both ions at a concentration of 1.00 mol dm⁻³ eg Cu²⁺/Cu⁺ would consist of platinum wire in a solution containing 1.00 mol dm⁻³ Cu²⁺ ions and 1.00 mol dm⁻³ Cu⁺ ions.

Calculating a standard cell potential by combining two electrode potentials

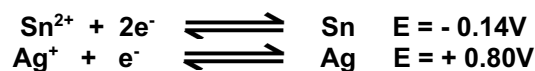
The standard cell potential (cell voltage) is the **difference** between the electrode potentials of the two half-cells, e.g.



The voltage of the cell is 0.32V, and zinc is the negative electrode. Sign is not needed.

Predicting the feasibility of a reaction e.g. Will tin reduce silver ions?

- The most positive half-reaction always goes to the right.
- One half-reaction goes in each direction.



Yes, tin reduces silver ions to silver atoms. Tin is oxidised to tin ions.



Limitations of predictions If E values differ by $> 0.30\text{V}$ a reaction proceeds even under non-standard conditions, but may be slow. **E values give no indication of rate.**

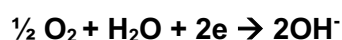
Changing concentration changes E values, e.g. for the Fe/Zn reaction above, increasing $[\text{Fe}^{2+}]$ shifts the equilibrium to the right, so the E value becomes more positive. The cell voltage therefore increases.

Storage and Fuel Cells

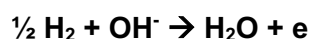
A fuel cell is a cell which converts the chemical energy of a continuous supply of reactants into electrical energy. Fuel is supplied at one electrode and oxygen to the other. A fuel cell uses the energy from the reaction of a fuel with oxygen to create a voltage.

Hydrogen-Oxygen Fuel Cell

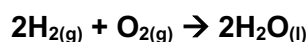
Oxygen diffuses through a porous **anode** and is reduced to OH^{-} .



Hydrogen diffuses through the porous **cathode**. When it comes into contact with the electrolyte, $\text{KOH}(\text{aq})$, absorbed H_2 is oxidized.



Overall reaction:



Scientists in the car industry are developing fuel cell vehicles (FCVs) fuelled by

- Hydrogen gas
- Hydrogen rich fuels (eg methanol, natural gas or petrol which are converted into hydrogen gas by an onboard 'reformer').

Advantages of FCVs over conventional petrol or diesel powered vehicles:

- Less pollution and less CO_2
- Greater efficiency in terms of energy output

Hydrogen can be stored in FCVs

1. As a liquid under pressure
2. **Adsorbed** on the surface of a solid material
3. **Absorbed** within a solid material

Limitations of hydrogen fuel cells

1. Storing and transporting hydrogen in terms on safety, feasibility of a pressured liquid and a limited life cycle of a solid 'adsorber' or 'absorber'.
2. Limited lifetime (requiring regular replacement and disposal) and high production costs
3. Use of toxic chemicals in their production

A 'hydrogen economy' may contribute largely to future energy needed but limitations include:

1. Public and political acceptance of hydrogen as a fuel
2. Handling and maintenance of hydrogen systems
3. Initial manufacture of hydrogen requiring energy