Electrochemistry

Oxidation states

The oxidation state of an element indicates the electron sharing in a compound. For example in H_2O hydrogen has an oxidation state of +1 and oxygen has an oxidation state of -2.

Oxidation state rules *in order*:

- If the species only has one element, use the rule that total oxidation number is equal the charge on the species
- Fluorine has an oxidation state of −1 in all its compounds
- Hydrogen has an oxidation state of +1 except in metal hydrides (-1)
- Oxygen has an oxidation state of −2 except in hydrogen peroxide (−1)
- Alkali metals (group I metals) are +1 and alkaline earth metals (group II metals) are +2
- Starting with the most electronegative, complete the rest such that the total oxidation number is equal to the total charge of the species (e.g. for SO_4^{2-} the total charge is 2-, so the oxidation number of S is +6)

A redox (reduction oxidation) reaction is a reaction in which *electrons are transferred*.
To determine whether a reaction is redox, calculate the oxidation state for each element on each side of the equation.
If an oxidation state decreases, that species has been *reduced* (gained electrons).
If an oxidation state increases, that species has been *oxidised* (lost electrons).

The species that is reduced is the oxidising agent, and the species that is oxidised is the reducing agent.

Electrochemical series and reactivity series

An electrochemical series shows the ability of species to be oxidised or reduced (act as reducing or oxidising agents).
A reactivity series is similar to an electrochemical series but only shows metals and does not always show both the reduced and oxidised forms. By convention the 'most reactive' metals (most easily oxidised) are shown at the top, and the 'least reactive' metals (most easily reduced) are shown at the bottom.
A metal is in its 'oxidised form' when it is an ion, and in its 'reduced form' when it is in elemental form.
A non-metal is in its 'reduced form' when it is an ion, and in its 'oxidised form' when it is in elemental form.
(*Remember:* an ion has oxidation state equal to its charge, an elemental form has zero oxidation state).

To predict whether two species will react:

1. Determine whether each species is currently in oxidised form or reduced form
2. Determine from the electrochemical series which species is more likely to be oxidised/reduced
3. If neither species is currently in the form determined in step 2, they will react to become so.

The further the two species are from each other in the electrochemical series, the more energetic the reaction.

Half-equations

Any redox reaction can be considered to consist of two half-reactions: one oxidation half-reaction, and one reduction half-reaction. The reduction half-reaction will have electrons on the left, and the oxidation half-reaction will have electrons on the right.
The half-reactions can be balanced separately and then combined. The following method can be used to balance a half-reaction:

1. Balance elements that are already on both sides
2. Balance the oxygen by adding water
3. Balance the hydrogen by adding H^+
4. Balance the charge by adding electrons

To combine the half-equations, multiply the species in each equation so that they have the same number of electrons, then combine all the species on each side. Don't forget to cancel out spectators.

Dichromate is a commonly used oxidising agent. It starts off orange and becomes reduced to green chromium ions. You must memorise the following unbalanced half equation (balance it when you use it):
$Cr_2O_7^{2-} \rightarrow Cr^{3+}$

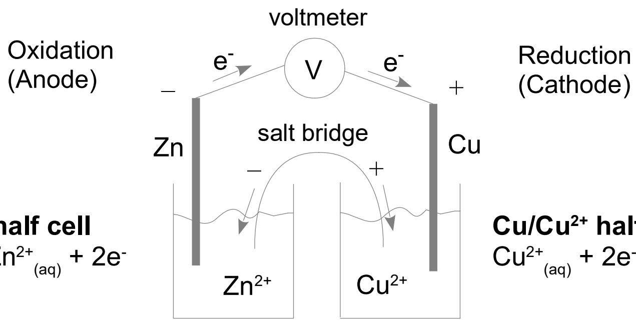
Electrochemical cells

An electrochemical cell either produces electricity by a chemical reaction or consumes electricity to cause a chemical reaction.

Galvanic (voltaic) cells produce an electric current from a spontaneous redox reaction. They consist of:

- *two half-cells*, with a different half-reaction occurring in each (one oxidation half-cell and one reduction half-cell)
- *electrolyte(s)*, the solution(s) found in the half-cells
- *a salt bridge*, to complete the circuit and allow ions to transfer and balance the charge lost or gained in each half-cell
- *electrodes*, one cathode (at which reduction occurs) and one anode (at which oxidation occurs)
  - In metal half cells, the electrodes are made of the metals that are participating in the half-reactions
  - In other half-cells the reactants are all contained in the solution and the electrodes are inert

The galvanic cell is connected to a circuit through which the electrons) flow. A voltmeter is often included in the circuit.
When a diagram of a galvanic cell is drawn, the charge at each electrode is shown (negative or positive), such that electrons are flowing from negative to positive.
(*Remember:* the electrons will flow from the more easily oxidised species to the more easily reduced species)



Zn/Zn²⁺ half cell
$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

Cu/Cu²⁺ half cell
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

Full redox equation:
$Zn(s) + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

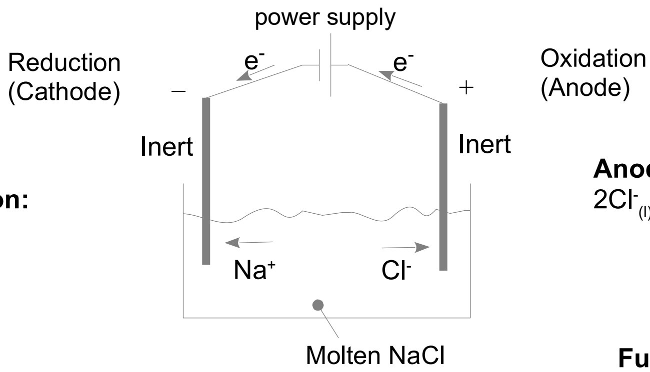
Electrolytic cells use an electric current from an external source to force a non-spontaneous redox reaction. They consist of:

- *one reaction vessel,* in which both half-reactions occur
- *an electrolyte*, the ions in this are attracted to the electrodes. This can be either a solution or molten ionic compound
- *inert electrodes*, one cathode (at which reduction occurs) and one anode (at which oxidation occurs)
- *an external power source,* which gives the cathode a negative charge (electrons) and the anode a positive charge

The electrodes must be inert (not involved in the reaction) or else they may be oxidised/reduced in preference to the ions in the electrolyte. Examples of inert electrode materials are platinum and graphite (carbon).

Electrolysis is the process by which electric current is passed through an electrolyte and products form.
To determine which products form, compare all the species in the solution or melt on the electrochemical series.
(*Remember:* species that are already in their oxidised form will not be oxidised, and species in their reduced form will not be reduced. Polyatomic anions like nitrate and sulphate are already in their oxidised form, so water is oxidised instead).

Some products cannot be obtained by electrolysis of a solution because water is oxidised or reduced instead. In these cases, the ionic compound must be melted (which requires very large amounts of energy due to the high melting point) and electrolysis is performed on the melt.



Cathode reaction:
$Na^+_{(l)} + e^- \rightarrow Na_{(l)}$

Anode reaction:
$2Cl^-_{(l)} \rightarrow Cl_{2\,(g)} + 2e^-$

Full redox equation:
$2Na^+_{(l)} + 2Cl^-_{(l)} \rightarrow 2Na_{(l)} + Cl_{2\,(g)}$