

REDOX and ELECTRODE POTENTIALS

OXIDISING AND REDUCING AGENTS

Remember that **oxidation** is loss of electrons and **reduction** is gain of electrons. Electrons cannot leave without somewhere to go.

- An **oxidising agent** accepts electrons. By gaining electrons, it becomes reduced.
- A **reducing agent** donates electrons. In losing electrons it becomes oxidised.

EXAM TIP

Redox reactions must have both an oxidising and a reducing agent.

OXIDATION STATES

In a compound, oxidation states must add up to zero. In a compound ion (e.g. NO_3^-), they must add up to the charge.

There are some oxidation states you need to know:

- H is +1 in almost all compounds
- O is -2 in almost all compounds (except in peroxides such as H_2O_2 , where O is in oxidation state -1)
- All pure elements have an oxidation number of 0

e.g. in Fe_2O_3 , say the oxidation state of iron = x , then $2x + (3 \times -2) = 0$ and $x = 3$ (this is called iron(III) oxide – the Roman numeral III in the name shows the oxidation state of iron)

REDOX EQUATIONS

A redox reaction can be represented by two **half-equations** – one for the reaction of the oxidising agent and one for the reaction of the reducing agent. Half-equations can be combined to form a full equation if the number of electrons is the same in both.

Mn oxidation number = +7
($7 - 4 \times 2 = -1$)

Mn oxidation number = +2
 $7 - 2 = 5$ so 5 e^- are gained

Example: Manganate(VII) ions are an oxidising agent: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ and iron(II) ions are a reducing agent: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$. They combine to form: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$

5Fe^{2+} in order to make 5 e^- (both half-equations must have the same number of electrons)

EXAM TIP

If you are asked to construct an equation, O and H can often be made to balance using H_2O

EXAM TIP

In the overall equation, the increase in oxidation state of the reducing agent must equal the decrease in oxidation state of the oxidising agent.

ELECTRODE POTENTIALS

A standard electrode potential (or standard redox potential) is a measure of a chemical's tendency to be reduced. It has the symbol $E^\ominus$ and is measured in volts. $E^\ominus$ refers only to reduction. Since it is not possible to have reduction without oxidation, it is not possible to measure $E^\ominus$ directly. You can, however, measure the difference between two $E^\ominus$ values – one for each half equation in a redox reaction.

When a cell is set up, the cell potential is the difference between the $E^\ominus$ values of the chemicals in the electrodes. The chemical with the larger $E^\ominus$ value is reduced, the other oxidised. The cell potential is calculated using: $E_{\text{cell}} = E_{\text{reduced}}^\ominus - E_{\text{oxidised}}^\ominus$. (The electrode written on the left is where oxidation happens)

The standard conditions are concentrations of 1 mol dm^{-3} and a temperature of 298 K (which is equal to 25 °C), and any gases must be at a pressure of 100 kPa. If any of these conditions change, the $E^\ominus$ values will change.

The standard hydrogen electrode is a special half-cell that is defined as having $E^\ominus = 0$. It has H_2 gas bubbling over a Pt electrode in a solution of H^+ ions. All other electrode potentials are measured relative to this.

Cell potentials can be used to tell which direction a redox reaction will go in. Look up the $E^\ominus$ value for the chemical that you think is going to be reduced and subtract the $E^\ominus$ value for the chemical that you think will be oxidised to calculate E_{cell} . If it is positive, the reaction will go in the direction you expect. If not, you need to switch which chemical will be reduced and which will be oxidised.

Example: Use the data to determine if this reaction will proceed as written: $\text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)} \rightarrow \text{Cu(s)} + 2\text{Ag}^+(\text{aq})$



EXAM TIP

In questions where you need $E^\ominus$ values, they will be on the exam paper.

$E_{\text{cell}} = E_{\text{reduced}}^\ominus - E_{\text{oxidised}}^\ominus = 0.34 - 0.80 = -0.46$. This reaction will actually go the other way – it will be the Cu that is oxidised and the Ag^+ reduced. Remember this is only true under standard conditions. It is possible that a redox reaction will proceed in different directions at different temperatures or with solutions at different concentrations, especially in cases where $E^\ominus$ values for the two electrodes are quite similar.

HALF-EQUATIONS

A redox reaction can be represented by two **half-equations** – one for the reduction reaction and one for the oxidation reaction.

e.g. magnesium reacting with hydrochloric acid is a redox reaction



H is reduced:
ox. state changes from 1 to 0 (1e gained per H atom)

Reduction half equation:
 $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

H⁺ is the oxidising agent

Mg is oxidised:
ox. state changes from 0 to 2 (2e lost)

Oxidation half equation:
 $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$

Mg is the reducing agent

ELECTROCHEMICAL CELLS

An electrochemical cell consists of two containers with a conductor (metal or graphite) dipping into a solution. These conductors are called **electrodes** and are linked with a salt bridge, which lets ions move between them.

Cells can be described without having to draw a picture. You need to know what symbols to use and what they represent:

- A vertical line separates substances in different states (solids, liquids, solutions or gases)
- A comma separates different substances in the same state (e.g. mixed in the same solution)
- A double vertical line represents the salt bridge

For example: $\text{Zn} | \text{Zn}^{2+}(\text{aq}) || \text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}$ shows a piece of zinc metal dipping into a solution of Zn^{2+} ions, which is connected via a salt bridge to a solution of both Fe^{3+} and Fe^{2+} ions, with platinum metal dipped in.

The convention is to write half-equations for electrode reactions always as a **reduction**, e.g. $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$

In a redox reaction, however, one electrode reaction must be an oxidation and one a reduction. The convention is that the **left-hand electrode** is where **oxidation** happens, with **reduction** occurring in the **right-hand electrode**.

Electrons travel from the left-hand electrode to the right-hand electrode.

A list of electrode reactions in order of increasing size of $E^\ominus$ values is called an **electrochemical series**. Metals at the top of the list (with very negative $E^\ominus$ values) are the most reactive (most likely to be oxidised).

