RAFFLES INSTITUTION RAFFLES PROGRAMME - YEAR FOUR CHEMISTRY

ELECTROLYSIS AND SIMPLE ELECTRIC CELL

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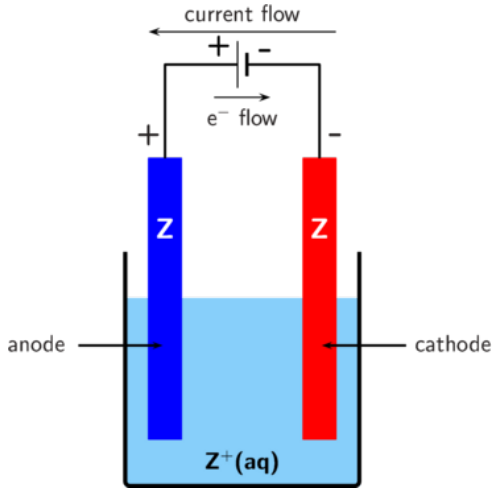
Electrolysis

The conduction of electricity by an ionic compound (electrolyte), when molten or dissolved in water, leading to the decomposition of the electrolyte.
i.e. Using an electric current to bring about chemical changes.

In an electrolytic cell, there are two **electrodes** immersed in an **electrolyte** and connected to a **battery / dry cell**.



The electrode connected to the positive terminal of the battery gains a positive charge. This **positive electrode** attracts negatively charged anions to it and is called the **anode**.
The electrode connected to the negative terminal of the battery gains a negative charge. This **negative electrode** attracts positively charge cations to it and is called the **cathode**.

The ions are discharged at the respective electrodes.
At the anode, **oxidation** occurs. Anions lose electrons. ($A^- \rightarrow A + e^-$)
At the cathode, **reduction** occurs. Cations gain electrons. ($C^+ + e^- \rightarrow C$)
Adding to the half-equations together gives us the overall electrolytic reaction. ($A^- + C^+ \rightarrow A + C$)
[To remember this, use **AN OX** and **RED CAT**. Also recall **OIL RIG** for redox reactions.]

The electrons liberated from the anions flow from the anode to cathode **through the wire**, carrying electricity with them (through the flow of mobile, free-moving electrons).
The cations then complete the electrical circuit by taking up the electrons.

Factors Affecting Electrolysis:

1. Ease of gaining/losing electrons. (Position in Electrochemical / Reactivity Series)
2. Concentration effect.
3. Nature of electrodes.

1. Ease of gaining/losing electrons

Electrochemical Series:	Cations	Anions
Increasing preferential	K+	
discharge down series	Ca2+	F-
	Na+	SO4 2-
	Mg2+	NO3-
	Al3+	
	Zn2+	
	Fe2+	
	Sn2+	Cl-
	Pb2+	Br-
	H+	I-
	Cu2+	OH-
	Ag+	
	Au+	

Note that while this series is not entirely the same as reactivity series, teachers are not going to be nitty gritty about the small details on what comes before what. The general idea is that a less reactive ion is more likely to be discharged, with reference to the general reactivities. For anions, hydroxide ions are discharged most of the times, and halides only in certain situations (elaborated below). Polyatomic (except hydroxide) ions and Fluoride ions are virtually never discharged. Remember to take note whether the electrolyte is in molten or aqueous state as well as be able to construct ionic equations for reactions occurring at both electrodes.

For cations, if M ion **gains electrons more readily** than N ion, then M ions are preferentially discharged/reduced.
For anions, if X ion **loses electrons more readily** than Y ion, then X ions are preferentially discharged/reduced.

2. Concentration Effect

Increasing the concentration of an ion promotes its discharge from solution. Only takes effect when the ions in question are closely positioned in the electrochemical series.
(For our syllabus, mainly used for questions with concentrated aqueous solution with halides, so concentration effect allows halides to be preferentially discharged/oxidized over hydroxide ion.)

3. Nature of the Electrode

Inert electrodes (Platinum and Carbon/Graphite) do not take part in the electrolytic reaction directly. However, side reactions may occur if the electrolytic product reacts with the electrode.
e.g. platinum with chlorine and carbon with liberated oxygen
Active electrodes (basically all other electrodes) can influence the ionic discharge by participating directly in the redox reaction.

Since oxidation occurs at the anode, a reactive anode (element) gets oxidized to form a cation instead of the anion getting oxidized. Electrolysis then proceeds as normal at the cathode.
Over time, the reactive anode becomes smaller in size/dissolves.

Purification/Refining of Metals

Impure metal made the anode, pure metal made cathode.
Metal atoms lose electrons and get oxidized to form metal ions in the electrolyte. These cations are attracted to the cathode and get reduced/discharged to from back as atoms, pure metal deposited on cathode. Normally this only works for metals below Hydrogen in the electrochemical series.

Anode becomes smaller, cathode becomes bigger, Electrolyte concentration constant.
Impurities on anode fall off and collect below the anode as anode slime.

Electroplating

Metal used to plate made anode, object to be plated made cathode.
Electrolyte contains metal cations of anode metal.
What happens for electrolysis is the same as in Purification/Refining of Metals

Layer of metal made anode found plated on object at cathode. Anode becomes smaller, Electrolyte concentration constant.

Non-conducting materials need a spray of metallic paint of graphite powder before electroplating.

Extraction (of Aluminum)

Bauxite ore which contains aluminum oxide and other impurities is purified to obtain pure aluminum oxide. Electrolysis yields aluminum.

Cathode [Reduction]: $Al^{3+}(l) + 3e^- \rightarrow Al(l)$
Anode [Oxidation]: $2O^{2-}(l) \rightarrow O_2(g) + 4e^-$
Add half-equations for overall reaction: $4Al^{3+}(l) + 6O^{2-}(l) \rightarrow 4Al(l) + 3O_2(g)$

Oxygen produced reacts with carbon anodes at high temperatures to form mainly carbon dioxide.
Carbon anodes must be replaced regularly.

Simple Electric Cell

A simple electric cell uses chemical reactions to produce electricity. It consists 2 electrodes (metals of **different reactivities**) immersed in an electrolyte.
When a wire connects the electrodes, electrons flow from the **more reactive** metal **to** the **less reactive** metal **through the wire** due to the potential difference between the 2 electrodes.

The more reactive metal (greater tendency to lose electrons) loses electrons, forming cations. This electrode is known as the anode and oxidation is occurring. [**OIL RIG AN OX RED CAT**]
$M \rightarrow M^+ + e^-$
We define this electrode as the negative electrode. (You can remember this by remembering that like charges repel, so this electrode is negative and repels the electrons away from it to the other electrode. This is NOT the correct theory and is just an easier way for you to remember how the electrodes are defined.)

The less reactive metal (smaller tendency to lose electrons) receives the electrons and passes them to the electrolyte. This electrode is known as the cathode and attracts cations in the electrolyte. These cations accept the electrons and are reduced.
$Y^+ + e^- \rightarrow Y$
We define this electrode as the positive electrode. (Likewise, this can be remembered as positive electrode and hence attracting electrons. However, this is NOT the correct explanation on how the simple cell works, just a way to remember.)

Note that the definition of the positive and negative electrode are different in a simple electric cell and electrolytic cell. However, **AN OX RED CAT** always applies. Refer to Summary.

Adding the two half-equations together gives us the overall electrolytic reaction: $M + Y^+ \rightarrow M^+ + Y$
Over time, the more reactive metal anode becomes smaller and smaller while at the less reactive metal cathode, a product is formed based on the ion discharged.

The greater the difference in reactivities of the two metal electrodes, the greater the voltage of the electric cell.

Summary

When answering a question about electrolysis or simple cell, always follow these steps:

1) Check for the presence of battery/dry cell. If battery present, electrolytic cell. If not, simple electric cell.

2) Label the electrodes positive, negative, cathode, anode, oxidation and reduction.
a. In an electrolytic cell, the positive and negative electrodes follow the battery terminals. Cathode is negatively charged and attracts cations. Anode is positively charged and attracts anions. Reduction occurs at the cathode and oxidation occurs at the anode.

b. In a simple electric cell, the negative electrode is the more reactive metal ('repels' the electron away) and the positive electrode is the less reactive metal ('attracts' the electron to it) because of their tendencies to lose electrons. Since the more reactive metal electrode loses electrons, oxidation occurs and this electrode is the anode. Cations are attracted to the less reactive metal electrode and take up the electrons to be discharged, reduction occurs and this is the cathode.

3) Identify what ions are present in the electrolyte, which electrode each of the ions will be attracted to and which ions will be discharged to form what product. Remember that the factors affecting these are: Reactivities, Concentration Effect (, and Nature of Electrodes for Electrolytic cell.)