Chem Factsheet

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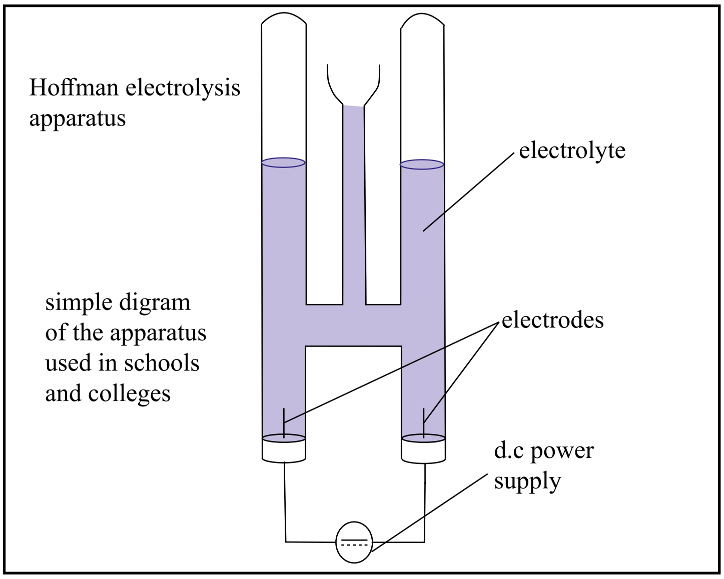
Electrolysis – An Electrode Potential Approach

Electrolysis involves the passing of a direct electric current through an ionic substance that is either molten or dissolved in a suitable solvent. It is a means of adding or removing electrons within a chemical system, leading to oxidation-reduction reactions. In 1785, Martinus van Marum first extracted tin, zinc, and antimony from their salts using electrolysis. Sir Humphry Davy (1778-1829) later used electrolysis to discover potassium, sodium, and other reactive elements, thus realising a new means for investigating chemistry. Modern uses of electrolysis include purifying metals and electroplating, e.g. chromium plating prolongs the use of materials due chromium's resistance to corrosion.

Electrolytic cells may require an external source of electrical energy to drive reactions that are not spontaneous. Fig. 1 describes the basic set up for the Hoffman Electrolysis Apparatus, which is used in schools and colleges to demonstrate the effect of electrolysis. The apparatus is partly filled with an electrolyte, which is a solution or gel containing ions. When the electric current is applied, redox half-reactions occur at each electrode.

Fig. 1



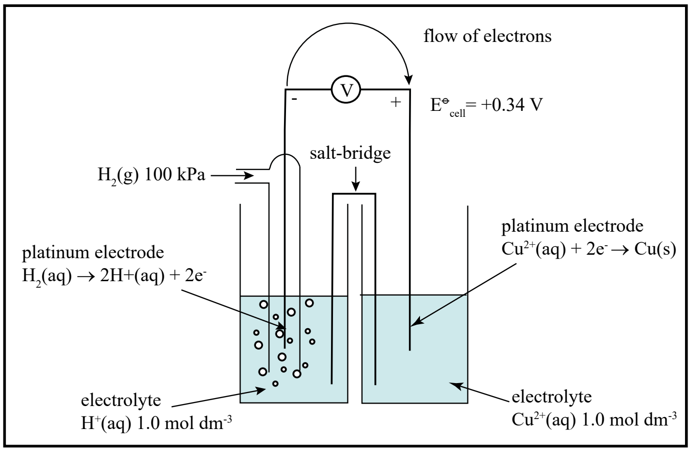
Standard Electrode Potential & The Electrochemical Series

To compare different redox equilibria, it is necessary to measure the redox potential for a given electrolyte cell with the standard hydrogen electrode under standard conditions.

Standard conditions: pressure 100 kPa; temperature 25 °C (298 K); concentration of ions in solution is 1.0 mol dm^{-3}.

Fig. 2 describes how the electrode potential of a redox equilibria half-cell is measured against the standard hydrogen electrode. Measuring the potential difference between the two half-cells is completed using a high resistance voltmeter. Any difference in charge between the two electrodes results in a flow of charge and electrons will move towards the positive electrode.

Fig. 2



To ensure a closed circuit, a salt-bridge connects the two half-cells. A salt-bridge typically consists of a saturated solution of potassium nitrate, KNO_3.

It is important to measure the maximum possible voltage available. This is called the electromotive force (emf). The symbol $E^{\ominus}_{cell}$ is used and is measured in volts, V. The standard hydrogen electrode is given as 0.00 V. This means that the electromotive force measured provides the electrode potential for the copper electrolyte cell. There are more electrons on the platinum electrode compared to the copper electrode. This is due to the formation of hydrogen ions, H^+. The fewer electrons on the copper electrode makes it is relatively more positive than the platinum electrode. The voltmeter will therefore record the electrode potential as positive.

$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	redox equilibria shifts towards oxidation (reverse direction)
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	redox equilibria shifts towards reduction (forward direction)

The electrode potential measured for the copper electrolyte is +0.34 V. An alternative short hand notation for representing electrolyte cells is provided below. Convention states that the sign for electrode potential, $E^{\ominus}_{cell}$, should match that of the right-side electrode.

$$Pt\ [H_2(g)]\ |\ 2H^+(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu(s) \qquad E^{\ominus}_{cell} = +0.34\ V$$

The collation of redox potentials for a range of redox equilibria gives the electrochemical series. Typically, the most negative $E^{\ominus}$ values are placed at the top of electrochemical tables and the most positive at the bottom. Table 1 gives the values of a small number of common values. Note the relationship between the $E^{\ominus}$ values and the means of extracting the metal from ores.

Table 1

Element	Equilibrium	$E^\ominus$ Values
potassium	$K^+(aq) + e^- \rightleftharpoons K(s)$	$E^\ominus_{cell} = -2.93$ V
calcium	$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	$E^\ominus_{cell} = -2.87$ V
sodium	$Na^+(aq) + e^- \rightleftharpoons Na(s)$	$E^\ominus_{cell} = -2.71$ V
magnesium	$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	$E^\ominus_{cell} = -2.37$ V
iron	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	$E^\ominus_{cell} = -0.44$ V
hydrogen	$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	$E^\ominus_{cell} = +0.00$ V
copper	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	$E^\ominus_{cell} = +0.34$ V
silver	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	$E^\ominus_{cell} = +0.80$ V

high reactivity abundant metals (potassium, calcium, sodium, magnesium)

high negative potential

electrolysis required to extract metal

low reactivity native metals (copper, silver)

positive potential

easy to extract (electrolysis not required

Electrode potentials are not absolute values. They are measured relative to the standard hydrogen electrode and are therefore relative to all other redox potentials. The more negative the redox potential is, the more the redox equilibrium shifts to oxidation and the greater the electrical energy required to overcome the high negative potential.

Redox Equilibria and Electrode Potentials

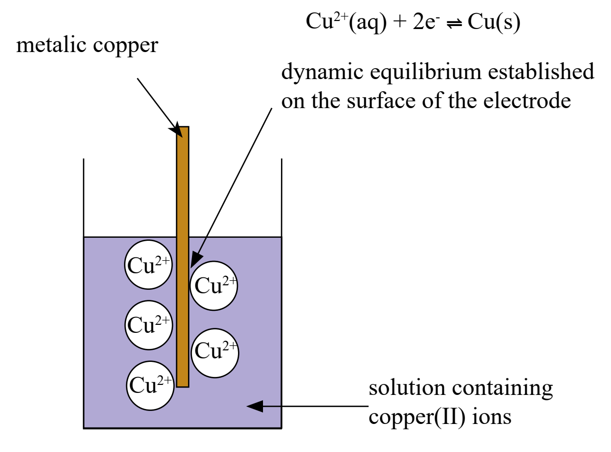
During redox reactions, chemical species losing electrons are said to be oxidised, while those gaining electrons are reduced. Electrolysis reactions are reversible and can be described as follows:

Reagents + Electrical Energy ⇌ Products

> Reversible reactions occur when products formed in a chemical reaction can react together to reform the original reactants.

The redox behaviour of metals, such as copper, are treated in terms of their chemical equilibria. In a copper electrolyte cell, a dynamic equilibrium is established, $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$, see Fig. 3. At equilibrium, the rate at which ions leave the surface is equal to the rate ions combine with the metal surface.

Fig. 3



> The standard convention for representing standard electrode potentials is to show the standard reduction potential in the forward direction.

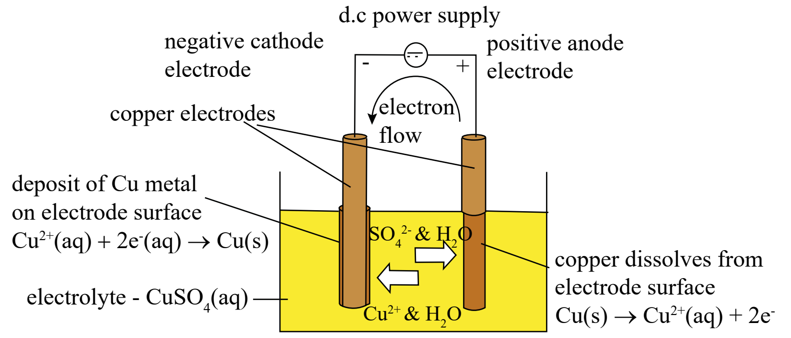
For example, $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$. The standard short-hand notation for the redox half-cell is, $Cu^{2+}|Cu$.

Fig. 4 describes the behaviour in a copper electrolyte cell when an electrical potential difference is applied across copper metal electrodes. The Cu^{2+} and ubiquitous water, H_2O, compete to gain electrons at the negative electrode. Successful reduction depends on the relative position of the species undergoing reduction in the electrochemical series. The standard electrode potential for the reduction of Cu^{2+} is more positive (greater tendency to occur) than that for the reduction of water to hydrogen gas.

$H_2O(l) + e^- \rightleftharpoons \frac{1}{2}H_2(g) + OH^-(aq)$	$E^\ominus = -0.83$ V
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	$E^\ominus = +0.34$ V

The more positive system has greater tendency to be reduced and gain electrons. Therefore, copper ions are reduced at the negative electrode and copper metal is deposited on the electrode. Copper(II) ions, Cu^{2+}, in contact with the surface of the electrode gain electrons and are reduced to metallic copper, Cu.

Fig. 4



Reaction at the cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

There is also competition at the positive electrode. When a copper electrode is used, it is easier for copper to oxidise and lose electrons than it is for the anion in solution, i.e., sulfate, SO_4^{2-}, or water to release electrons at the anode. On the surface of the anode, electrons are lost by metallic copper, Cu, which oxidises to form copper(II) ions, Cu^{2+}. This process is called electrode participation.

Reaction at the anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

$Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2e^-$ $\quad E^\ominus = -0.34\ V$
$H_2O(l) \rightleftharpoons \frac{1}{2}O_2(g) + 2H^+ + 2e^-$ $\quad E^\ominus = -1.23\ V$
$2SO_4^{2-}(aq) \rightleftharpoons S_2O_8^{2-}(aq) + 2e^-$ $\quad E^\ominus = -2.01\ V$

The standard electrode potential for the oxidation of copper metal is less negative than the oxidation of either water or the sulfate ion. Oxidation of copper, therefore, has a greater tendency to occur at the anode during electrolysis using copper electrodes.

The electrolysis of copper(II) sulphate solution using participating copper electrodes results with copper metal dissolved from the copper anode, copper metal plated on the copper cathode and the copper ion concentration in the aqueous electrolyte solution remaining constant. This method is used in the purification of copper, as only copper is deposited at the negative electrode. Electrolysis results with an increase in the mass of the copper cathode and a reduction of mass of the copper anode. This quantity is measured using the Faraday constant, F, that is, the electrical charge per mole of electrons (Faraday constant, F, = 96500 C mol^{-1}). Note that for the copper electrolyte cell, two moles of electrons are required to deposit one mole of copper atoms on the cathode.

In general, a metal will be deposited at the cathode if the reduction of its ions is more favourable (has a less negative/more positive electrode potential than that for water, -0.83 V). If this is not the case, then water with be reduced in preference and hydrogen gas will be discharged.
The same principle applies at the anode: if the oxidation potential of the anion is less negative/more positive than that for the oxidation of water, -1.23 V) then it is likely that the anion will be oxidised. This is typical for solutions of halide ions. If the oxidation of water is more favourable, then oxygen gas will be formed.

For example, in the electrolysis of aqueous sodium bromide:

Competing reactions at the cathode:
$Na^+(aq) + e^- \rightleftharpoons Na(s)$ $\quad E^\ominus = -2.71\ V$
$H_2O(l) + e^- \rightleftharpoons H_2(g) + OH^-(aq)$ $\quad E^\ominus = -0.83\ V$

The electrode potential for the reduction of sodium is more negative than that of water and so hydrogen will be discharged at the cathode.

Competing reactions at the anode:
$Br^-(aq) \rightleftharpoons \frac{1}{2}Br_2(g) + e^-$ $\quad E^\ominus = -1.09\ V$
$H_2O(l) \rightleftharpoons \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$ $\quad E^\ominus = -1.23\ V$

The electrode potential for the oxidation of bromide ions is less negative, and thus more favourable, than the oxidation of water. Bromine will be formed at the anode.

This idea can be used to predict whether or not a halogen or oxygen will be discharged during the electrolysis of a halide salt. The electrode potentials for the oxidations of the halide ions are:

$F^-(aq) \rightleftharpoons \frac{1}{2}F_2(g) + e^-$ $\quad E^\ominus = -2.87\ V$
$Cl^-(aq) \rightleftharpoons \frac{1}{2}Cl_2(g) + e^-$ $\quad E^\ominus = -1.36\ V$
$Br^-(aq) \rightleftharpoons \frac{1}{2}Br_2(l) + e^-$ $\quad E^\ominus = -1.09\ V$
$I^-(aq) \rightleftharpoons \frac{1}{2}I_2(s) + e^-$ $\quad E^\ominus = -0.54\ V$

It can be seen from this that fluorine can never be discharged from an aqueous solution as oxidation of fluoride ions has a very low tendency to occur. Conversely, electrolysis of bromide or iodide solutions should always result in the production of the halogen. The situation with chlorine is a little more complicated as the relative ease of oxidation of chloride ions compared to water depends on the concentration of ions present (see below). Typically, concentrated solutions yield chlorine whilst dilute solutions yield oxygen.

The Nature of Electrodes on Electrolysis Products

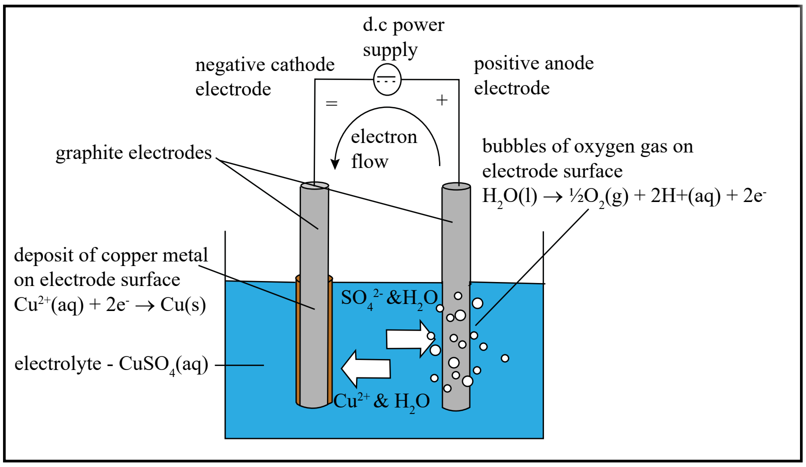
The products formed during the electrolysis of aqueous solutions are effected by the nature of the electrodes used. For example, replacing participating electrodes with inert platinum or graphite electrodes may alter the products formed at the electrodes. Fig. 5 describes the behaviour in a copper electrolyte cell when an electrical potential difference is applied across two inert graphite electrodes. At the positive electrode, species compete to lose electrons. Species that have less negative or more positive oxidation potentials are more likely to undergo oxidation at the anode.

If the copper electrodes previously used in the electrolysis of copper(II) sulfate are changed to graphite, then the following oxidation reactions compete at the anode.

$H_2O(l) \rightleftharpoons \frac{1}{2}O_2(g) + 2H^+ + 2e^-$ $\quad E^\ominus = -1.23\ V$
$2SO_4^{2-}(aq) \rightleftharpoons S_2O_8^{2-}(aq) + 2e^-$ $\quad E^\ominus = -2.01\ V$

The less negative electrode potential will tend towards oxidation. Water is easier to oxidise than sulfate ions and so oxygen gas is discharged at the anode; bubbling is observed.

Fig. 5

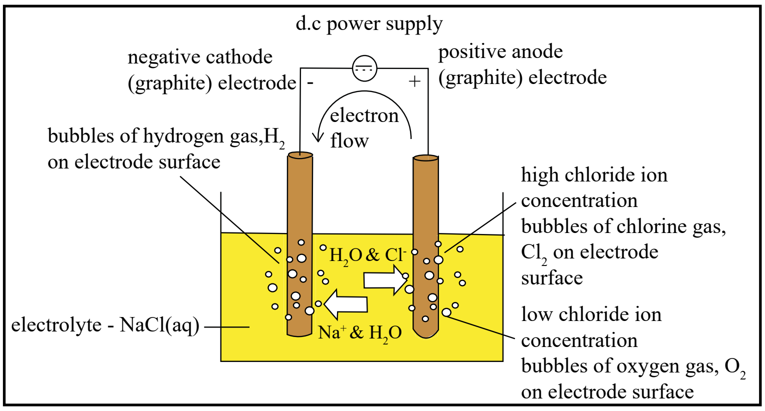


The Effect of Ion Concentration on Electrolysis Products

The competition of anions in electrolytes and the preferential selection of ions releasing electrons at the positive electrode depends on relative positions in the electrochemical series and relative concentrations of ions in the electrolyte. An increase in the concentration of an anion tends to promote the release of electrons from that anion. Electrode potential data suggests water molecules are preferentially oxidised ($E^\ominus = -1.23\ V$) over chloride ions, Cl^- ($E^\ominus = -1.36\ V$). However, if the electrolyte solution contains a high halide ion concentration this leads to the preferential release of electrons from the halide ions over water molecules and the production of the chlorine at the anode.

Fig. 6 describes the contrasting behaviour at the anode for electrolytes of different sodium chloride concentration.

Fig. 6



Brine solutions contain a minimum of 3.5% sodium chloride. During the electrolysis of brine, chlorine gas is produced at the positive electrode, i.e. in high chloride ion, Cl^-, concentrations, the chlorine ion preferentially releases electrons at the positive electrode.

Reaction at the anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

In low chloride ion, Cl^-, concentrations, water molecules are preferentially released and oxygen gas is produced at the positive electrode.

Reaction at the anode: $H_2O(l) \rightarrow ½O_2(g) + 2H^+(aq) + 2e^-$

The precise reasons for the concentration-dependent discharge of chlorine at the anode are complex and are not required in Sixth Form syllabuses. Briefly, the electrode potentials that we have been using to compare the tendency for redox processes to occur are all standardised; one of the requirements is 1.00 mol dm^{-3} solutions of ions. As the concentration of the chloride ions changes, the electrode potential for their oxidation also changes. The value becomes less negative as the concentration increases (i.e., the value gets closer to that for the oxidation of water). In addition, water is more difficult to oxidise at the anode than predicted due to a phenomenon called overpotential.

Using Electrolysis

Electrolysis is used to extract metals from minerals and ores, e.g. aluminium, sodium, potassium, magnesium, and calcium. The conductivity of copper is improved using electrolysis to refine copper from low purity copper. The industrial processes using electrolysis includes the production of chlorine, sodium hydroxide, and sodium chlorate. Electrolysis is used to produce oxygen in nuclear submarines and in spacecraft. It is also used in cleaning and preserving metal artefacts and old coins. It is also used to remove rust from old engine parts. Electrolysis is used in electroplating. This involves depositing a thin film of metal over an object. This is completed for practical or decorative purposes, e.g. coins or in the production of cheap jewellery.

Questions

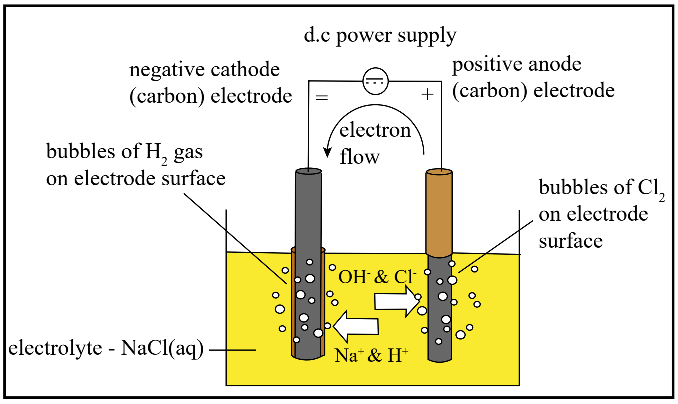
1. Ions successfully released at the electrodes depend on which three factors?
2. A solution of potassium iodide undergoes electrolysis. State which of the following statements are true. If a statement is incorrect, provide a correct alternative statement.
   (a) Hydrogen gas is being produced at the cathode and iodine at the anode.
   (b) Potassium ions are reduced to potassium atoms at the cathode.
   (c) A brown colour is observed at one of the electrodes due to this half-reaction: $2H_2O + 4I^- \rightarrow 2I_2 + 2OH^- + H_2 + 2e^-$
3. A sodium chloride electrolyte solution (brine) undergoes electrolysis. There is a high concentration of sodium ions, Na^+, and chloride ions, Cl^-. There are low concentrations of hydrogen ions, H^+, and hydroxide ions, OH^-, due to the ionisation of water.
   (a) Sketch and label a simple diagram describing the electrode reactions and products of the electrolysis.
   (b) Complete redox half-equations for the reactions occurring at both electrodes. Identify if the reaction is oxidation or reduction.
   (c) Write an overall chemical equation for the electrolysis of brine, sodium chloride solution.
4. (a) During an electroplating experiment, a steel cathode is used. The electrolyte used is a solution of nickel(II) sulphate. What should the anode be made of to successfully complete the experiment?
   (b) Complete the redox half-equation for the cathode during the electroplating of steel with nickel.

Answers

1 The relative positions of competing species in the electrochemical series.
The nature/composition of the electrodes.
The concentration of competing species in the electrolyte.

2. (a) True
   (b) False – Iodine ions are oxidised at the anode.
   (c) False – A brown colour is observed at the anode due to:
   $2I^- \rightarrow I_2 + 2e^-$

3. (a)



(b) At cathode
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ (reduction)
At anode $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ (oxidation)
(c) $2NaCl(aq) + 2H_2O(l) \rightarrow H_2(g) + Cl_2(g) + 2NaOH(aq)$

4 (a) Nickel
(b) $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

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