

SECTION 15

ELECTROCHEMISTRY

Some systems involving redox reactions can be designed so that the reactants (and products) are partially separated from each other, and the reaction leads to an electric current being produced in an external circuit, and which can be used for many useful purposes. Batteries and their many uses are the obvious examples. Electrical energy can also be used to drive non-spontaneous chemical reactions to produce desired products in processes known as electrolysis. This section introduces the language and concepts of these processes collectively known as electrochemistry.

Electrochemistry: The branch of chemistry that covers the relative strengths of oxidants and reductants, the production of electric current from chemical reactions, and the use of electricity to produce chemical change.

Electrochemical cell: A system made up of two electrodes in contact with an electrolyte.

Electrode: A conductor of electricity, commonly a metal or graphite in contact with an **electrolyte** in an electrochemical cell.

Electrolyte: A medium (phase) which conducts electricity by the movement of ions [e.g. a molten salt] or a substance which dissolves in a solvent to give a conducting solution [e.g. aqueous sodium chloride, NaCl or any other soluble ionic compound].

Electrode reaction: A chemical reaction occurring at an electrode involving gain or loss of electrons. It is called a **half-reaction**. [e.g. $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$; $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$]
(See *page 12-4*.)

Redox couple: The two species of a half- reaction involving oxidation or reduction. (See *page 12-3*.) Represented as oxidised species/reduced species [e.g. Cu^{2+}/Cu ; Cl_2/Cl^- ; $\text{Fe}^{3+}/\text{Fe}^{2+}$].

Half-cell: An electrode and the couple it is in contact with [e.g. $\text{Zn}(\text{s})|\text{Zn}^{2+}(\text{aq})$, a zinc rod in contact with an aqueous solution containing zinc cations; $\text{Fe}^{3+}(\text{aq}),\text{Fe}^{2+}(\text{aq})|\text{Pt}$, a platinum rod in contact with an aqueous solution containing ferric and ferrous ions]. The electrode may be one of the species of the couple or an inert species [e.g. zinc and platinum respectively above]. The vertical line represents a phase boundary.

Galvanic cell: an electrochemical cell that produces electricity from a chemical reaction. It consists of two half-cells connected by a junction [e.g. a membrane (diaphragm) or salt bridge] allowing ions to be transferred between the electrolytes of the two half-cells. When the electrodes are connected externally by a conductor electrons flow through the conductor from the negative electrode to the positive electrode. It is normally represented by two half-cells separated by a double vertical line representing the junction allowing transfer of ions. [e.g. $\text{Zn}(\text{s})|\text{Zn}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu}(\text{s})$ or more simply as $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$ if it is clear from the context that aqueous solutions are involved.]

Cell potential or electromotive force: symbol E , the electric potential difference between the electrodes of a galvanic cell when no current is flowing. In the above representation of a galvanic cell it is the **electrode potential** of the right hand electrode minus the **electrode**

potential of the left hand electrode. It is normal to show the negative electrode on the left and the positive electrode on the right and thus express the cell potential as a positive quantity. The SI unit of E is the volt, symbol V.

Standard hydrogen electrode: symbol *she*, a reference electrode defined as having zero electrode potential. It consists of a platinum electrode in contact with gaseous dihydrogen and aqueous hydronium ions under defined conditions.

Electrode potential (of a couple): symbol $E(\text{oxidised form/reduced form})$, also called **reduction potential** or **redox potential** is the electrode potential of that couple relative to the standard hydrogen electrode. More precisely it is the cell potential of a galvanic cell in which one half-cell is the standard hydrogen electrode, and is negative if the electrode of the couple is the negative electrode of that cell and positive if the electrode is the positive electrode of that cell [e.g. $E(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$; $E(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$; $E(\text{Cl}_2/\text{Cl}^-) = 1.40 \text{ V}$].

The magnitude of a redox potential is a measure of the relative strength of an oxidant or reductant. The more positive the redox potential the stronger the oxidant (i.e. the greater its potential to oxidise some other species) and the weaker the reductant. Conversely the more negative the redox potential the stronger the reductant and the weaker the oxidant.

Strong oxidant: An oxidant of a redox couple with a large positive redox potential [e.g. F_2 , $E(\text{F}_2/\text{F}^-) = 2.9 \text{ V}$; $\text{Cr}_2\text{O}_7^{2-}$, $E(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = 1.4 \text{ V}$. The half-reaction corresponding to this couple in aqueous solution is that given on page 12-5,
 $14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$].

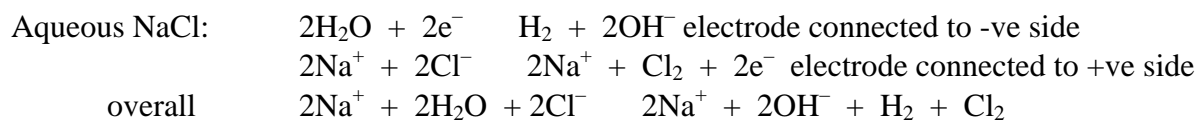
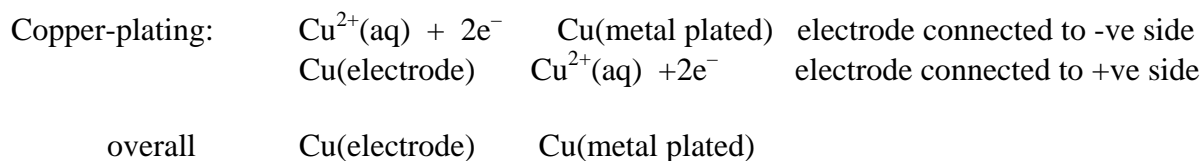
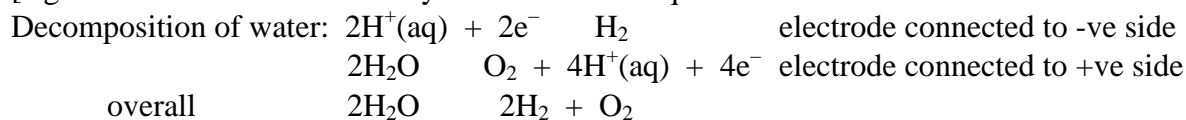
Strong reductant: a reductant of a redox couple with a large negative redox potential [e.g. Na, $E(\text{Na}^+/\text{Na}) = -2.71 \text{ V}$].

and the overall reaction the sum of these, $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$].

Electrolysis: the use of electric current to drive chemical reactions. Electrical energy is converted into potential chemical energy, and the non-spontaneous reaction is forced to occur.

Electrolytic cell: an electrochemical cell for electrolysis. Consists of two electrodes in contact with electrolyte(s), one connected to the positive side and one connected to the negative side of a direct current power supply. A species is oxidised at the electrode connected to the positive side (electrons are "sucked" out of the electrode) and a species is reduced at the electrode connected to the negative side (electrons are "pushed" in). The design of cell varies. The electrodes may both be in the same electrolyte [e.g. in decomposition of water from aqueous sulfuric acid, or copper-plating a metal from a copper sulfate solution and a copper electrode] or in different compartments separated by a device allowing migration of ions between the two electrolytes [e.g. the production of H_2 , Cl_2 and NaOH from the electrolysis of aqueous NaCl]. As for a galvanic cell, half-reaction equations and an overall chemical equation can be written for the cell reactions.

[e.g. for the above three electrolytic reactions the equations are as follows:

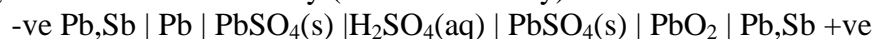


Here Na^+ ions migrate through a diaphragm from the compartment where Cl_2 is being produced to the compartment where H_2 is being produced.]

Anode: the electrode at which a species is oxidised. Thus for a galvanic cell it is the negative electrode, and for an electrolysis cell it is the electrode connected to the positive side of the power supply.

Cathode: the electrode at which a species is reduced. Thus for a galvanic cell it is the positive electrode, and for an electrolysis cell it is the electrode connected to the negative side of the power supply.

Reversible galvanic cell: a cell in which the direction of the cell reaction can be reversed by electrolysis [e.g. the common car battery (lead-acid battery)



Pb,Sb represents the electrodes, a grid made of an alloy which supports the reductant, Pb , and the oxidant, PbO_2 . To recharge the battery electrons are pushed into the left-hand electrode and sucked out of the right-hand electrode by applying an external power supply].

Faraday's laws of electrochemistry: The 1st law states that the mass of the substance being oxidised or reduced is proportional to the charge passed. The 2nd law states that this mass is directly proportional to the molar mass of the substance and inversely proportional to its

