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. $Cu^{2+} + 2e^- \rightarrow Cu$; $Zn \rightarrow Zn^{2+} + 2e^-$] (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^-; Fe^{3+}/Fe^{2+}].

Half-cell: An electrode and the couple it is in contact with [e.g. $Zn(s) |Zn^{2+}(aq)$, a zinc rod in contact with an aqueous solution containing zinc cations; $Fe^{3+}(aq),Fe^{2+}(aq)|Pt$, 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. $Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$ or more simply as $Zn|Zn^{2+}||Cu^{2+}|Cu$ 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(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. $E(Cu^{2+}/Cu = 0.34$ V; $E(Zn^{2+}/Zn) = -0.76$ V; $E(Cl_2/Cl^-) = 1.40$ 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, $E(F_2/F^-) = 2.9$ V; $Cr_2O_7^{2-}$, $E(Cr_2O_7^{2-}/Cr^{3+})$ 1.4 V. The half-reaction corresponding to this couple in aqueous solution is that given on *page 12-5*,
$14H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$].

Strong reductant: a reductant of a redox couple with a large negative redox potential [e.g. Na, $E(Na^+/Na) = -2.7$ V].

Table of electrode potentials: A table listing the electrode potentials of redox couples. As electrons flow spontaneously from the negative to the positive electrode the electrode potentials can be used to deduce the direction of a redox reaction. [e.g. Can Cl_2 oxidise copper, Cu? Since this reaction would involve flow of electrons from Cu to Cl_2 it can be seen from the electrode potentials above that the redox reaction can occur as $E(Cu^{2+}/Cu)$ is negative with respect to $E(Cl_2/Cl^-)$. A table in which the electrode potentials increase down the table (most negative at the top and most positive at the bottom) can be regarded as an energy diagram. A spontaneous reaction involving two couples will be that in which electrons lose energy by moving from a reductant of one couple to the oxidant of another couple below it in the table.

[e.g.

Couple	E/V
Zn^{2+}/Zn	-0.76
Cu^{2+}/Cu	0.34
Cl_2/Cl^-	1.40

Electrons can flow from Zn to Cu^{2+} but not from Cu to Zn^{2+}. Thus zinc metal can reduce copper ions to copper metal but copper metal cannot reduce zinc ions to zinc metal.]

Cell reaction: The overall chemical redox reaction occurring in the cell. What distinguishes a cell reaction from a general redox reaction is that the reactants are physically separated in the cell and the processes of oxidation and reduction are accompanied by electron flow in an external conductor [e.g. for the cell $Zn^{2+}|Zn||Cu^{2+}|Cu$ the half-reactions will be:

$$Zn \rightarrow Zn^{2+} + 2e^- \quad \text{(as the zinc electrode is negative)}$$
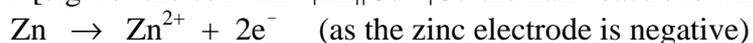
and $$Cu^{2+} + 2e^- \rightarrow Cu \quad \text{(as copper is the positive electrode)}$$

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

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:
Decomposition of water: $2H^+(aq) + 2e^- \rightarrow H_2$ $\quad\quad\quad$ electrode connected to -ve side
$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $2H_2O \rightarrow O_2 + 4H^+(aq) + 4e^-$ electrode connected to +ve side
$\quad\quad$ overall $\quad\quad\quad\quad\quad$ $2H_2O \rightarrow 2H_2 + O_2$

Copper-plating: $\quad\quad\quad$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(\text{metal plated})$ electrode connected to -ve side
$\quad\quad\quad\quad\quad\quad\quad\quad$ $Cu(\text{electrode}) \rightarrow Cu^{2+}(aq) + 2e^-$ $\quad\quad$ electrode connected to +ve side

$\quad\quad$ overall $\quad\quad\quad\quad$ $Cu(\text{electrode}) \rightarrow Cu(\text{metal plated})$

Aqueous NaCl: $\quad\quad\quad$ $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ electrode connected to -ve side
$\quad\quad\quad\quad\quad\quad\quad\quad$ $2Na^+ + 2Cl^- \rightarrow 2Na^+ + Cl_2 + 2e^-$ electrode connected to +ve side
$\quad\quad$ overall $\quad\quad\quad\quad$ $2Na^+ + 2H_2O + 2Cl^- \rightarrow 2Na^+ + 2OH^- + H_2 + Cl_2$
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)
$\quad\quad\quad\quad\quad$ -ve Pb,Sb | Pb | $PbSO_4(s)$ |$H_2SO_4(aq)$ | $PbSO_4(s)$ | PbO_2 | Pb,Sb +ve
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].
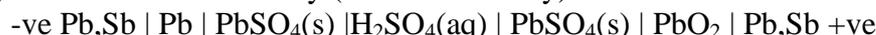
Faraday's laws of electrochemistry: The 1st law states that the mass of the substance being oxidised or reduced is proportional to the charge passed. The 2nd law states that this mass is directly proportional to the molar mass of the substance and inversely proportional to its

change in oxidation state, z. Combining these laws the charge passed, $Q \propto zm/M$ ($Q \propto zn$), i.e. $Q = znF$ where Q is the charge passed, n is the amount of substance oxidised or reduced and F is the proportionality constant, called the **Faraday constant**.
When $z = 1$ and $n = 1$ mol, $Q = 1$ mol x $F = F$ mol, i.e. the Faraday constant is the charge per mole of electrons.

Faraday constant: symbol F, the molar electric charge, i.e. the charge per mole of electrons, 96 485 C mol^{-1}.

EXERCISES

Couple	Half-reaction	E/V
Zn^{2+}/Zn	$Zn^{2+} + 2e^- \rightleftarrows Zn$	-0.76
Sn^{2+}/Sn	$Sn^{2+} + 2e^- \rightleftarrows Sn$	-0.14
Cu^{2+}/Cu	$Cu^{2+} + 2e^- \rightleftarrows Cu$	0.34
I_2/I^-	$I_2 + 2e^- \rightleftarrows 2I^-$	0.54
Fe^{3+}/Fe^{2+}	$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	0.77
Ag^+/Ag	$Ag^+ + e^- \rightleftarrows Ag$	0.80
Br_2/Br^-	$Br_2 + 2e^- \rightleftarrows 2Br^-$	1.10
O_2/H_2O	$O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$	1.23
Cl_2/Cl^-	$Cl_2 + 2e^- \rightleftarrows 2Cl^-$	1.40

From the above table

1.   Deduce which of the following species is the strongest oxidant: I_2, Ag^+, Sn^{2+}, O_2

2.   Deduce which of the following species is the strongest reductant: Cl^-, Sn, Ag, Fe^{2+}

Write the cell, the chemical equation for the overall cell reaction and determine the cell potential for a galvanic cell made from the redox couples:

3. Zn^{2+}/Zn and Fe^{3+}/Fe^{2+} 4. Br_2/Br^- and I_2/I^- 5. Ag^+/Ag and Cl_2/Cl^-

Predict whether

6. Sn can reduce Br_2 7. O_2 can oxidise Cl^- 8. Ag can reduce Cu^{2+}

9. Fe^{3+} can oxidise I^-