3 Electrochemistry

Electrochemistry

Electrochemistry is the chemistry of reactions that involve electron transfer.

In **spontaneous** reactions, electrons are released with energy that can be used in **electrochemical cells**. In **non-spontaneous** reactions, electrons have to be supplied with energy in order to produce chemicals that are wanted in **electrolytic cells** or **electrolysis.**

In both electrochemical and electrolytic cells the terms *anode* and *cathode* have the following meanings:

Anode: The electrode where **oxidation** is occurring.

Cathode: The electrode where **reduction** is occurring.

Anode and **oxidation** both start with vowels.
Cathode and **reduction** both start with consonants.

Electrochemical cells

REVISION

3A 1 Electrochemical cells key facts

Quiz 3A 1

If zinc powder is put into copper nitrate solution, a redox reaction occurs:

$$Zn(s) + Cu(NO_3)_2(aq) \longrightarrow Zn(NO_3)_2(aq) + Cu(s)$$

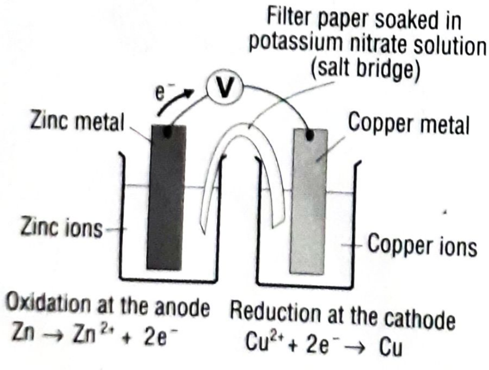
Energy is lost in the form of heat.

Since this is a redox reaction we can write it as two half-equations:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

These two half-equations can occur in separate beakers, provided there is a path for the electrons to travel (a wire), and a path for the ions to travel (a salt bridge).



A zinc electrode is placed in a beaker containing zinc nitrate solution. Beside it is a beaker containing a copper electrode in copper nitrate solution. A piece of filter paper soaked in potassium nitrate solution connects the beakers. Before the two electrodes are connected by wire, the metal atoms are in equilibrium with the metal ions in their respective beakers. The position of each equilibrium will depend on the temperature and concentration of each solution. When the wire connects the electrodes, electrons can flow from the zinc to the copper (shown by the voltmeter), leaving behind Zn^{2+} ions in the zinc beaker, and forming Cu atoms in the copper beaker. Potassium ions enter the copper beaker and nitrate ions enter the zinc beaker to keep the system electrically neutral.

The flow of electrons in the wire is an electric current. We call each beaker a **half-cell**. 200 years ago Humphry Davy did the first electrolysis experiments using electricity generated by piles of zinc and silver discs, separated by filter paper soaked in sulfuric acid. A series of cells connected together is called a **battery**.

PRACTICAL

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ENCOUNTER

3A John Frederic Daniell

Standard electrode potentials

The voltage produced by a given combination of half-cells depends on the willingness for one cell to lose electrons (be oxidised) and the other cell to gain electrons (be reduced). When two half-cells are connected with a voltmeter, chemists say they are measuring the **electromotive force (emf** or *E*) of the cell. We can therefore use emf figures to compare the strength of oxidising and reducing agents.

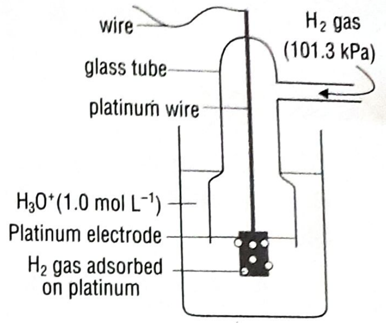
The equilibrium reaction in each half-cell is affected by concentration, so clearly the actual emf of a given combination of half-cells is affected by both the redox power of the reagents and the concentrations of their solutions. If we want to compare the strengths of oxidising and reducing agents we must test them under the same conditions of concentration, temperature and pressure.

POWERPOINT

3A Practical electrochemical cells

The standard half-cell

Oxidation will not occur without reduction, so it is impossible to find the emf of a single half-cell (eg Cl_2/Cl^-). If each half-cell is to have a meaningful number, we must measure the emf of that half-cell relative to a common half-cell. The **standard half-cell** is the H^+/H_2 half-cell—chosen because about half the redox reagents oxidise it, and the other half reduce it. This cell is defined as having an emf of zero. The standard hydrogen half-cell is shown on the left.



The standard hydrogen electrode.

Standard conditions for emf measurements are:

- All elements are in pure form
- Temperature 25 °C or 298 K
- All concentrations 1.0 mol L^{-1}
- Pressure of gases 1.0 atm or 101.3 kPa

For half-cells such as this one that have no solid conducting reagent that can act as an electrode, an electrode must be added. In this case platinum is chosen, but graphite is also used as an inert electrode for many half-cells.

Standard electrode potentials ($E°$) for each substance are found by putting the hydrogen half-cell on the right-hand side and connecting the positive terminal of the voltmeter to that cell. They are also called **standard reduction potentials**.

Cell diagrams

When an electrochemical cell is set up, and the voltage measured, the voltmeter will give a positive or negative value, depending on which way round the terminals of the voltmeter are connected. Obviously, if we are going to use the cell emf readings we have to know which way round the readings were taken. One way would be to draw a picture of the set-ups shown above, but that would be far too time-consuming and take up too much space. Instead, a special IUPAC convention (a set of agreed rules) is used to write a 'cell diagram' of the cell.

In the zinc/copper cell opposite, the zinc half-cell is on the left, and the copper half-cell is on the right. The cell diagram of this system is as follows:

$$Zn(s) / Zn^{2+}(aq) // Cu^{2+}(aq) / Cu(s)$$

It does not matter initially which electrode system is chosen for the left-hand or right-hand side but this convention is agreed to:

- a double line (//) represents the salt bridge or other device separating the two cells
- a single line (/) represents a change of phase, with the two phases in direct contact
- if two species are both present in a single solution, we separate them with a comma
- write the left-hand electrode first
- write the left-hand cell as oxidation (ie, write the reduced form first, then the oxidised form)
- write the right-hand side as reduction (ie, write the oxidised form first, then the reduced form)
- write the right-hand electrode last.

Reduction on the **R**ight (both begin with **R**) Oxidation on the Left

Practical electrochemical cells

The lead-acid battery

The common car battery is a set of six electrochemical cells, each generating about 2 volts, connected in series. Each cell consists of alternating plates of lead and lead dioxide immersed in an aqueous solution of sulfuric acid which acts as the electrolyte. When the cell is supplying current, the lead metal is oxidised to Pb^{2+} and the PbO_2 is reduced to Pb^{2+}:

Anode (negative electrode):

$$Pb(s) - 2e^- \longrightarrow Pb^{2+}(aq)$$

Cathode (positive electrode):

$$PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$$

The $Pb^{2+}(aq)$ produced reacts with the sulfuric acid to form a precipitate of lead sulfate which builds up on the plates:

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$$

The concentration of sulfuric acid in the cells decreases as the cell goes flat. Since the density of concentrated sulfuric acid is almost twice that of water (1.98 g/mL), a density measurement on the acid will give a good ndication of how flat the battery is.

The feature which distinguishes the lead-acid battery from most other commercially available electrochemical cells is that the above reactions

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3C The lead-acid

can be reversed. By passing an electric current back through the cell, the Pb^{2+} can be converted to Pb and PbO_2:

$$2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)$$

A car battery provides the energy needed to start the engine. Once it is running the engine turns the alternator which generates electricity to recharge the battery. After many repeated charge-discharge cycles, some of the $PbSO_4$ falls to the bottom of the container and the H_2SO_4 concentration remains correspondingly low. The battery can no longer be recharged fully. It should be traded in for a new one, and the lead recovered and reused to make new batteries.

ENCOUNTER

3C Vanadium flow battery

The dry cell (Leclanché cell)

The common dry cell or torch battery (non-rechargeable) consists of:

- a zinc case, which is the negative electrode
- a central graphite electrode, which is the positive electrode
- black manganese dioxide powder held around the central electrode in a paste
- an electrolyte paste of NH_4Cl, $ZnCl_2$ and water
- a physical separator between the electrodes, such as paper or muslin.

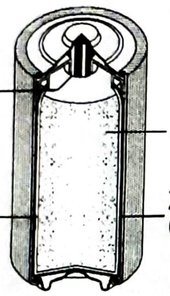
When the cell is generating electricity, the zinc is oxidised to $Zn^{2+}(aq)$ and the MnO_2 is reduced to the Mn(III) compound $Mn(OH)_3$.

Anode (negative electrode):

$$Zn(s) - 2e^- \longrightarrow Zn^{2+}(aq)$$

Cathode (positive electrode):

$$MnO_2(s) + NH_4^+(aq) + H_2O + e^- \longrightarrow Mn(OH)_3(s) + NH_3(aq)$$



The traditional 'zinc-carbon' cell has a central carbon electrode (+); a paste mix containing the $NH_4Cl/ZnCl_2$ electrolyte and the MnO_2 oxidising agent; a paper separator and a zinc case which acts as the negative electrode.

It is not possible to use acid as the electrolyte because the acid would dissolve the zinc. Instead acidic salts are used, which provide sufficient $H^+(aq)$ for the reduction of MnO_2 without dissolving the case. The ammonia that is produced forms a complex with the Zn^{2+}.

Alkaline dry cells are similar to ordinary dry cells, except that the electrolyte is alkaline because it contains KOH instead of NH_4Cl and the inner surface of the zinc case is roughened to give a larger surface area.

The cathode reaction is different:

$$2MnO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq)$$

Quiz 3C 1

The voltage of an alkaline dry cell is slightly lower than the standard cell (1.4 V rather than 1.5 V), but the voltage stays constant for the life of the cell, instead of gradually decreasing like the Leclanché cell.

Test yourself 3C Practical electrochemical cells

1 In the lead-acid battery, during discharge:
 a what species is oxidised? ______
 b what species is reduced? ______

2 Why does the density of the acid solution in a lead-acid battery decrease as the battery discharges?
______
______

3 In the common dry cell (Leclanché cell):
 a what species is oxidised? ______
 b what species is reduced? ______
 c what is the function of the carbon? ______