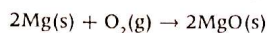


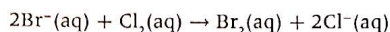
## Redox reactions (1)

### DEFINITIONS OF OXIDATION AND REDUCTION

Oxidation used to be narrowly defined as the addition of oxygen to a substance. For example, when magnesium is burned in air the magnesium is oxidized to magnesium oxide.

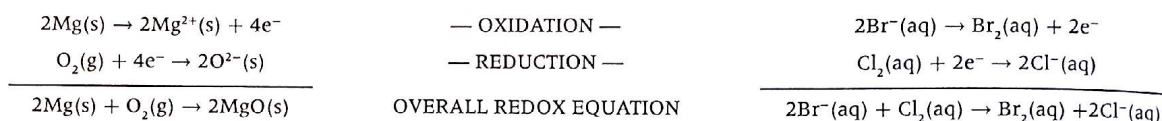


The electronic configuration of magnesium is  $[\text{Ne}]3s^2$ . During the oxidation process it loses two electrons to form the  $\text{Mg}^{2+}$  ion with the electronic configuration of  $[\text{Ne}]$ . **Oxidation** is now defined as the *loss of one or more electrons from a substance*. This is a much broader definition, as it does not necessarily involve oxygen. Bromide ions, for example, are oxidized by chlorine to form bromine.



If a substance loses electrons then something else must be gaining electrons. *The gain of one or more electrons is called reduction*. In the first example oxygen is reduced as it is gaining two electrons from magnesium to form the oxide ion  $\text{O}^{2-}$ . Similarly, in the second example chlorine is reduced as each chlorine atom gains one electron from a bromide ion to form a chloride ion.

Since the processes involve the transfer of electrons oxidation and reduction must occur simultaneously. Such reactions are known as **redox reactions**. In order to distinguish between the two processes half-equations are often used:

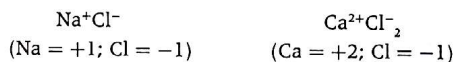


Understanding that magnesium must lose electrons and oxygen must gain electrons when magnesium oxide  $\text{MgO}$  is formed from its elements is a good way to remember the definitions of oxidation and reduction. Some students prefer to use the mnemonic OILRIG: **O**xidation **I**s the **L**oss of electrons, **R**eduction **I**s the **G**ain of electrons.

### RULES FOR DETERMINING OXIDATION STATES

It is not always easy to see how electrons have been transferred in redox processes. Oxidation states can be a useful tool to identify which species have been oxidized and which reduced. Oxidation states are assigned according to a set of rules:

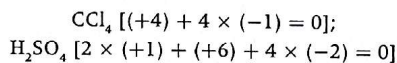
- In an ionic compound between two elements the oxidation state of each element is equal to the charge carried by the ion, e.g.



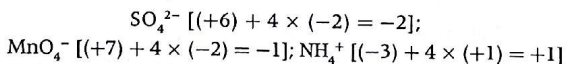
- For covalent compounds assume the compound is ionic with the more electronegative element forming the negative ion, e.g.



- The algebraic sum of all the oxidation states in a compound = zero, e.g.

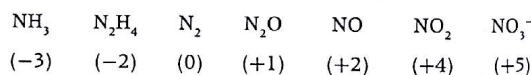


- The algebraic sum of all the oxidation states in an ion = the charge on the ion, e.g.



- Elements not combined with other elements have an oxidation state of zero, e.g.  $\text{O}_2$ ;  $\text{P}_4$ ;  $\text{S}_8$ .
- Oxygen when combined always has an oxidation state of -2 except in peroxides (e.g.  $\text{H}_2\text{O}_2$ ) when it is -1.
- Hydrogen when combined always has an oxidation state of +1 except in certain metal hydrides (e.g.  $\text{NaH}$ ) when it is -1.

Many elements can show different oxidation states in different compounds, e.g. nitrogen in:



When elements show more than one oxidation state the oxidation number is represented by using Roman numerals when naming the compound,

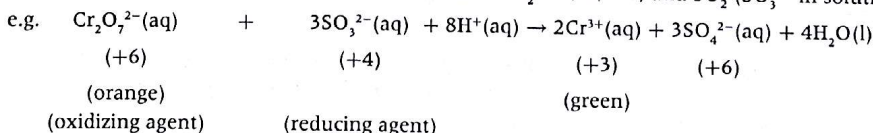
e.g.  $\text{FeCl}_2$  iron(II) chloride;  $\text{FeCl}_3$  iron(III) chloride  
 $\text{K}_2\text{Cr}_2\text{O}_7$  potassium dichromate(VI);  $\text{KMnO}_4$  potassium manganate(VII)  
 $\text{Cu}_2\text{O}$  copper(I) oxide;  $\text{CuO}$  copper(II) oxide.

### OXIDIZING AND REDUCING AGENTS

A substance that readily oxidizes other substances is known as an **oxidizing agent**. Oxidizing agents are thus substances that readily accept electrons. Usually they contain elements that are in their highest oxidation state,

e.g.  $\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{F}_2$ ,  $\text{SO}_3$  ( $\text{SO}_4^{2-}$  in solution),  $\text{MnO}_4^-$ , and  $\text{Cr}_2\text{O}_7^{2-}$ .

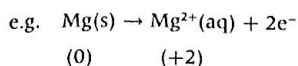
Reducing agents readily donate electrons and include  $\text{H}_2$ , Na, C, CO, and  $\text{SO}_2$  ( $\text{SO}_3^{2-}$  in solution),



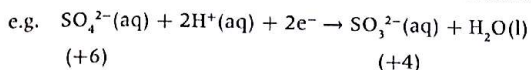
## Redox reactions (2)

## OXIDATION AND REDUCTION IN TERMS OF OXIDATION STATES

When an element is oxidized its oxidation state *increases*.



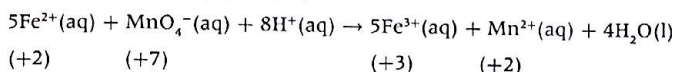
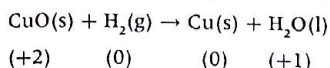
When an element is reduced its oxidation state *decreases*.



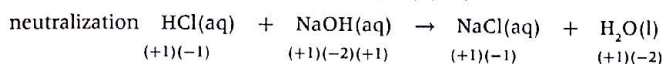
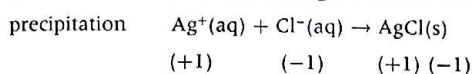
The change in the oxidation state will be equal to the number of electrons involved in the half-equation.

Using oxidation states makes it easy to identify whether or not a reaction is a redox reaction.

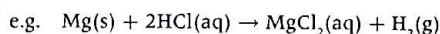
### Redox reactions (change in oxidation states)



Not redox reactions (no change in oxidation states)

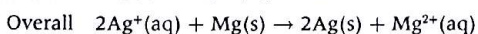
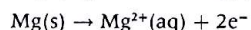
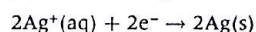


Note: reactions where an element is uncombined on one side of the equation and combined on the other side *must* be redox reactions since there must be a change in oxidation state,



## BALANCING REDOX EQUATIONS

To obtain the overall redox equation the number of electrons in the oxidation half-equation must balance the number of electrons in the reduction half-equation. For many redox equations this is straightforward. For example, the oxidation of magnesium by silver(I) ions. Write the two half-equations, then double the silver half-equation so that both half-equations involve two electrons and then simply add them together:



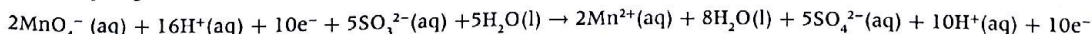
It is less straightforward when there is a change in the number of oxygen atoms in a compound or ion. **The rule is that if oxygen atoms need to be accounted for then water is used and if hydrogen atoms need to be accounted for then hydrogen ions,  $\text{H}^+(\text{aq})$ , are used.** Consider the oxidation of sulfite ions,  $\text{SO}_3^{2-}(\text{aq})$  to sulfate ions,  $\text{SO}_4^{2-}(\text{aq})$  by purple permanganate(VII) ions,  $\text{MnO}_4^-(\text{aq})$ , which are reduced to very pale pink (virtually colourless)  $\text{Mn}^{2+}(\text{aq})$  ions in the process.

$\text{SO}_3^{2-}(\text{aq}) \rightarrow \text{SO}_4^{2-}(\text{aq})$ . Add the extra O atom by adding water and ensure the charges on both sides are equal so the balanced half-equation becomes:  $\text{SO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{SO}_4^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^-$

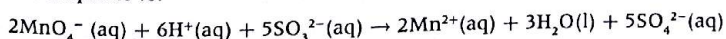
$\text{MnO}_4^-(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq})$ . Add  $8\text{H}^+$  ions to remove the oxygen atoms as water and ensure the charges on both sides are equal so the balanced half-equation becomes:  $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$ .

Note that the number of electrons can also be obtained from the change in oxidation states. S goes from +4 to +6 so two electrons are involved and Mn goes from +7 to +2 so five electrons are involved.

To ensure both half-equations have the same number of electrons multiply the sulfite equation by 5 and the permanganate(VII) equation by 2 then obtain the overall redox equation by adding them together to cancel out the ten electrons and simplify the water and hydrogen ions.



Which simplifies to:



This means that acid ( $H^+$  ions) needs to be present for the reaction to take place.



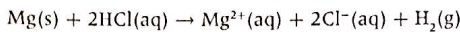
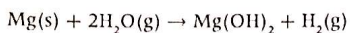
# Activity series and Winkler method

## ACTIVITY SERIES

Lithium, sodium and potassium all react with cold water to give similar products but the reactivity increases down the group.

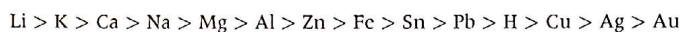


Slightly less reactive metals react with steam and will give hydrogen with dilute acids, e.g.

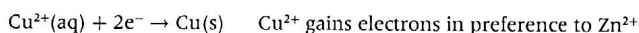
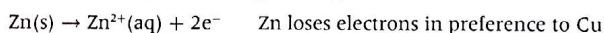
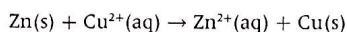


In all of these reactions the metal is losing electrons – that is, it is being oxidized and in the process it is acting as a reducing agent. An activity series of reducing agents can be deduced by considering the reactivity of metals with water and acids, and the reactions of metals with the ions of other metals.

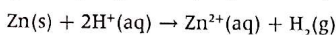
The series used by the IB can be found in Section 25 of the IB Chemistry data booklet. A simplified series follows the order:



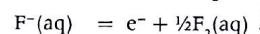
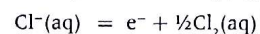
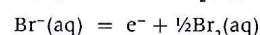
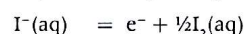
Generally the more readily the metal ion loses its outer electron(s) the more reactive it is although note that lithium is actually higher than potassium in the activity series as the redox reactions also involve the hydration of the ions formed. Metals higher in the series can displace metal ions lower in the series from solution, e.g. zinc can react with copper ions to form zinc ions and precipitate copper metal.



This also explains why only metals above hydrogen can react with acids (displace hydrogen ions) to produce hydrogen gas, e.g.

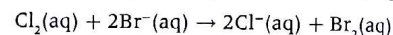


The series can be extended for oxidizing agents. The most reactive oxidizing agent will be the species that gains electrons the most readily. For example, in group 17



increasing  
oxidizing  
ability

Oxidizing agents lower in the series gain electrons from species higher in the series, e.g.

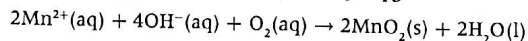


## WINKLER METHOD

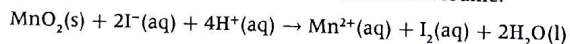
One application of a redox process is the Winkler method which is used to measure Biological Oxygen Demand (BOD). BOD is a measure of the dissolved oxygen (in ppm) required to decompose the organic matter in water biologically over a set time period, which is usually five days. Polluted water with a high BOD without the means of replenishing oxygen will not sustain aquatic life.

The sample of the water is saturated with oxygen so the initial concentration of dissolved oxygen is known. A measured volume of the sample is then incubated at a fixed temperature for five days while microorganisms in the water oxidize the organic material. An excess of a manganese(II) salt is then added to the sample.

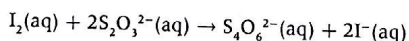
Under alkaline conditions manganese(II) ions are oxidized to manganese(IV) oxide by the remaining oxygen.



Potassium iodide is then added which is oxidized by the manganese(IV) oxide in acidic solution to form iodine.



The iodine released is then titrated with standard sodium thiosulfate solution.



By knowing the amount (in mol) of iodine produced the amount of oxygen present in the sample of water can be calculated and hence its concentration.

### Worked example

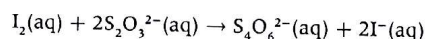
100 cm<sup>3</sup> of a sample of water was treated with an excess of alkaline manganese(II) sulphate, MnSO<sub>4</sub>(aq). After all the dissolved oxygen had reacted the solution was then acidified

and excess potassium iodide. KI(aq) added. The iodine released was titrated with sodium thiosulfate solution, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq), using starch as an indicator. It was found that 6.00 cm<sup>3</sup> of 1.00 × 10<sup>-2</sup> mol dm<sup>-3</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq) was required to react with all the iodine. Determine the concentration of dissolved oxygen in parts per million (ppm).

**Step 1.** Calculate the amount of sodium thiosulfate used in the titration.

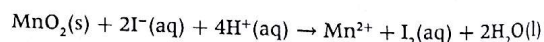
$$\text{Amount of } S_2O_3^{2-}(aq) = \frac{6.00}{1000} \times 1.00 \times 10^{-2} = 6.00 \times 10^{-5} \text{ mol}$$

**Step 2.** Calculate the amount of iodine that reacted with the sodium thiosulfate.



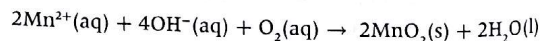
$$\text{Amount of } I_2(aq) = \frac{1}{2} \times 6.00 \times 10^{-5} = 3 \times 10^{-5} \text{ mol}$$

**Step 3.** Calculate the amount of MnO<sub>2</sub> produced by the oxidation of the Mn<sup>2+</sup> ions.



$$\text{Amount of } MnO_2 = 3 \times 10^{-5} \text{ mol}$$

**Step 4.** Calculate the mass of oxygen dissolved in the 100 cm<sup>3</sup> sample of water.



$$\text{Amount of } O_2 = \frac{1}{2} \times 3 \times 10^{-5} = 1.5 \times 10^{-5} \text{ mol}$$

$$\text{Mass of } O_2 = 32.00 \times 1.5 \times 10^{-5} = 4.8 \times 10^{-4} \text{ g}$$

**Step 5.** Calculate the concentration of dissolved oxygen in parts per million (ppm). (This is the same as the mass in mg dissolved in 1 dm<sup>3</sup> of water.)

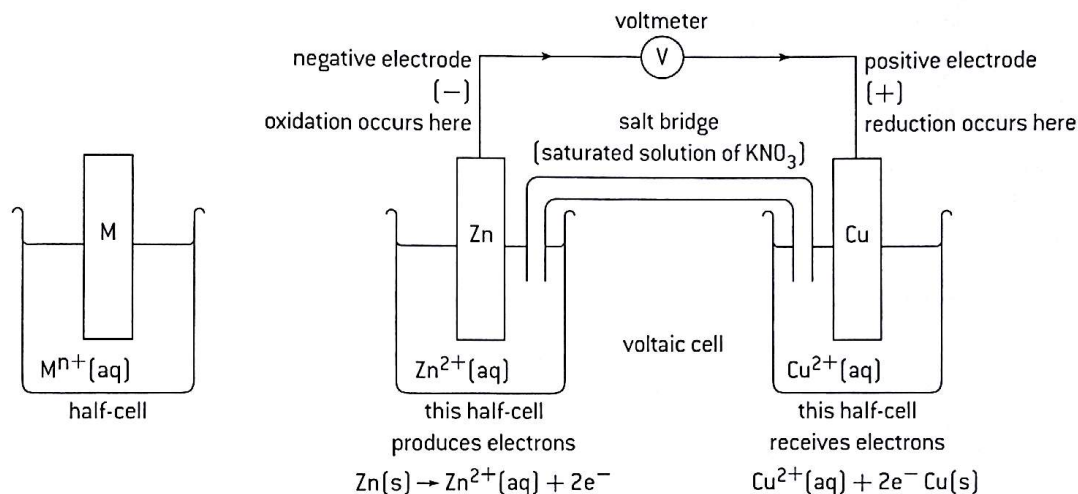
$$100 \text{ cm}^3 \text{ contains } 4.8 \times 10^{-4} \text{ g of } O_2 \text{ so concentration} \\ = 4.8 \times 10^{-3} \text{ g dm}^{-3} = 4.8 \text{ ppm.}$$

# Electrochemical cells

## SIMPLE VOLTAIC CELLS

A half-cell is simply a metal in contact with an aqueous solution of its own ions. A voltaic cell consists of two different half-cells, connected together to enable the electrons transferred during the redox reaction to produce energy in the form of electricity. The cells are connected by an external wire and by a salt bridge, which allows the free movement of ions.

A good example of a voltaic cell is a zinc half-cell connected to a copper half-cell. Because zinc is higher in the activity series the electrons will flow from the zinc half-cell towards the copper half-cell. To complete the circuit and to keep the half-cells electrically neutral, ions will flow through the salt bridge. The voltage produced by a voltaic cell depends on the relative difference between the two metals in the activity series. Thus the voltage from a  $\text{Mg(s)}/\text{Mg}^{2+}(\text{aq})$  half-cell connected to a  $\text{Cu(s)}/\text{Cu}^{2+}(\text{aq})$  half-cell will be greater than that obtained from a  $\text{Zn(s)}/\text{Zn}^{2+}(\text{aq})$  half-cell connected to a  $\text{Fe(s)}/\text{Fe}^{2+}(\text{aq})$  half-cell.



## CONVENTION FOR WRITING CELLS

By convention in a cell diagram the half-cell undergoing oxidation is placed on the left of the diagram and the half-cell undergoing reduction on the right of the diagram. The two aqueous solutions are then placed either side of the salt bridge e.g.



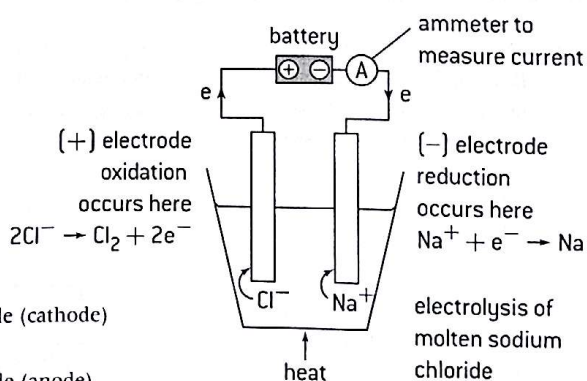
The words cathode and anode can also be used to describe the electrodes. The anode is where oxidation occurs so for a voltaic cell it is the negative electrode but for an electrolytic cell (see below), where the electricity is provided from an external source, the anode is the positive electrode, which can cause some confusion.

## ELECTROLYTIC CELLS

In a voltaic cell electricity is produced by the spontaneous redox reaction taking place. Electrolytic cells are used to make non-spontaneous redox reactions occur by providing energy in the form of electricity from an external source. In an electrolytic cell electricity is passed through an **electrolyte** and electrical energy is converted into chemical energy. An electrolyte is a substance which does not conduct electricity when solid, but does conduct electricity when molten or in aqueous solution and is chemically decomposed in the process. A simple example of an electrolytic cell is the electrolysis of molten sodium chloride.

- During the electrolysis:
- sodium is formed at the negative electrode (cathode)  
 $\text{Na}^+(\text{l}) + \text{e}^- \rightarrow \text{Na(l)}$  reduction
  - chlorine is formed at the positive electrode (anode)  
 $2\text{Cl}^-(\text{l}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$  oxidation
  - The current is due to the movement of electrons in the external circuit and the movement of ions in the electrolyte.

Electrolysis is an important industrial process used to obtain reactive metals, such as sodium, from their common ores.





## FACTORS AFFECTING THE DISCHARGE OF IONS DURING ELECTROLYSIS

During the electrolysis of molten salts there are only usually two ions present, so the cation will be discharged at the negative electrode (cathode) and the anion at the positive electrode (anode). However, for aqueous electrolytes there will also be hydrogen ions and hydroxide ions from the water present. There are three main factors that influence which ions will be discharged at their respective electrodes.

### 1. Position in the electrochemical series

The lower the metal ion is in the electrochemical series the more readily it will gain electrons (be reduced) to form the metal at the cathode. Thus in the electrolysis of a solution of sodium hydroxide, hydrogen will be evolved at the negative electrode in preference to sodium, whereas in a solution of copper(II) sulfate, copper will be deposited at the negative electrode in preference to hydrogen.

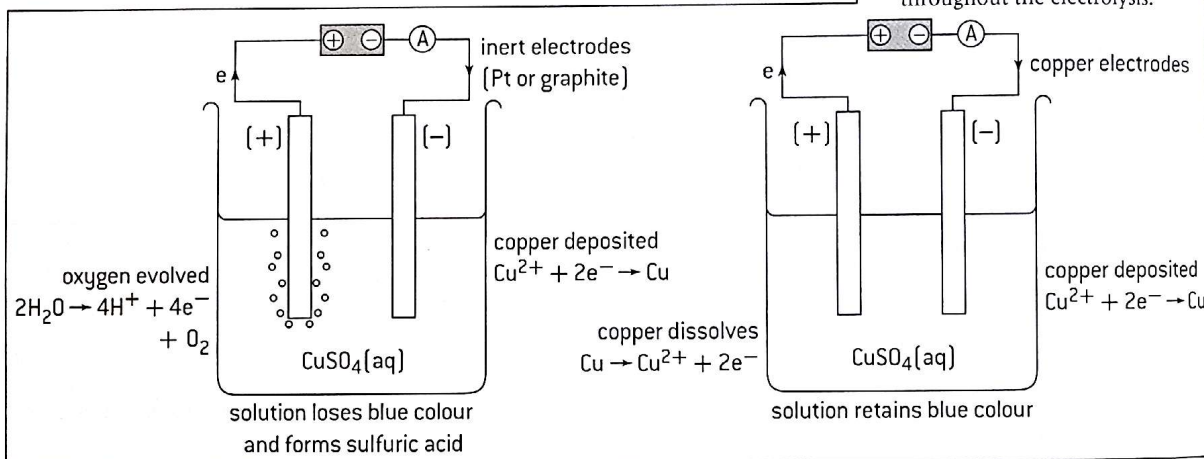
For negative ions the order of discharge follows  $\text{OH}^- > \text{Cl}^- > \text{SO}_4^{2-}$ .

### 2. Concentration

If one of the ions is much more concentrated than another ion then it may be preferentially discharged. For example, when electricity is passed through an aqueous solution of sodium chloride both oxygen and chlorine are evolved at the positive electrode. For dilute solutions mainly oxygen is evolved, but for concentrated solutions of sodium chloride more chlorine than oxygen is evolved.

### 3. The nature of the electrode

It is normally safe to assume that the electrode is inert, i.e. does not play any part in the reaction. However, if copper electrodes are used during the electrolysis of a solution of copper sulfate then the positive electrode is itself oxidized to release electrons and form copper(II) ions. Since copper is simultaneously deposited at the negative electrode the concentration of the solution will remain constant throughout the electrolysis.



## FACTORS AFFECTING THE QUANTITY OF PRODUCTS DISCHARGED DURING ELECTROLYSIS

The amount of substance deposited will depend on:

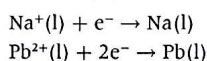
- The number of electrons flowing through the system, i.e. the amount of charge passed. This in turn depends on the current and the time for which it flows. If the current is doubled then twice as many electrons pass through the system and twice as much product will be formed. Similarly if the time is doubled twice as many electrons will pass through the system and twice as much product will be formed.

$$\text{charge} = \text{current} \times \text{time}$$

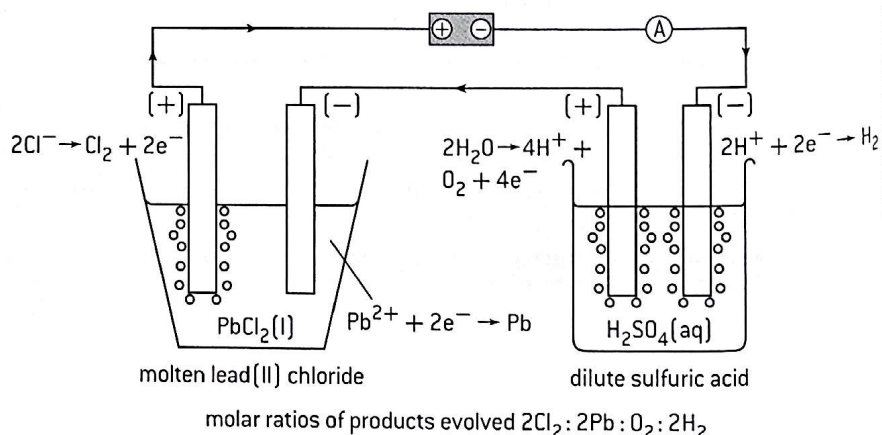
(1 coulomb = 1 ampere  $\times$  1 second)

- The charge on the ion. To form one mole of sodium in the electrolysis of molten sodium chloride requires one mole of electrons to flow

through the cell. However, the formation of one mole of lead during the electrolysis of molten lead(II) bromide requires two moles of electrons.



If cells are connected in series then the same amount of electricity will pass through both cells and the relative amounts of products obtained can be determined.



# HL Electroplating and standard electrode potentials

## ELECTROPLATING

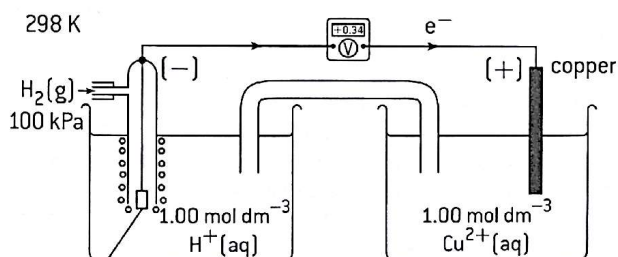
Electrolysis can also be used in industry to coat one metal with a thin layer of another metal. This process is known as **electroplating**.

For example, in copper plating the negative electrode (cathode) is made from the metal to be copper plated. It is placed into a solution of copper(II) sulfate together with a positive electrode (anode) made from a piece of copper. As electricity is passed through the solution the copper anode dissolves in the solution to form  $\text{Cu}^{2+}(\text{aq})$  ions and the  $\text{Cu}^{2+}(\text{aq})$  ions in solution are deposited onto the cathode. By making the anode of impure copper and the cathode from a small piece of pure copper this process can also be used to purify impure copper. This is an important industrial process as one of the main uses of copper is for electrical wiring, where purity is important since impure copper has a much higher electrical resistance.

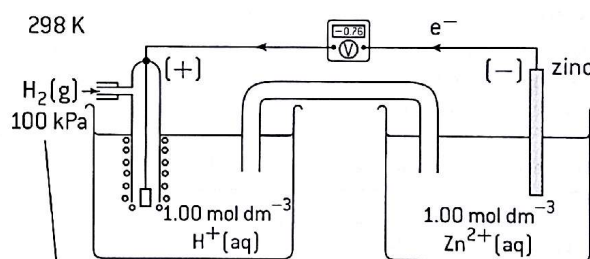
## STANDARD ELECTRODE POTENTIALS

There are two opposing tendencies in a half-cell. The metal may dissolve in the solution of its own ions to leave the metal with a negative potential compared with the solution, or the metal ions may deposit on the metal, which will give the metal a positive potential compared with the solution. It is impossible to measure this potential, as any attempt to do so interferes with the system being investigated. However, the electrode potential of one half-cell can be compared against another half-cell. The hydrogen half-cell is normally used as the standard. Under standard conditions of 100 kPa pressure, 298 K, and  $1.0 \text{ mol dm}^{-3}$  hydrogen ion concentration the standard electrode potential of the hydrogen electrode is assigned a value of zero volts.

When the half-cell contains a metal above hydrogen in the reactivity series electrons flow from the half-cell to the hydrogen electrode, and the electrode potential is given a negative value. If the half-cell contains a metal below hydrogen in the reactivity series electrons flow from the hydrogen electrode to the half-cell, and the electrode potential has a positive value. The standard electrode potentials are arranged in increasing order to form the electrochemical series.



The platinum electrode is coated with finely divided platinum, which serves as a catalyst for the electrode reaction.



pressure just above 100 kPa so  $\text{H}_2$  can escape from electrode

## ELECTROCHEMICAL SERIES

(A more complete series can be found in the IB data booklet)

Couple	$E^\ominus / \text{V}$
$\text{K(s)}/\text{K}^+(\text{aq})$	-2.93
$\text{Ca(s)}/\text{Ca}^{2+}(\text{aq})$	-2.87
$\text{Na(s)}/\text{Na}^+(\text{aq})$	-2.71
$\text{Mg(s)}/\text{Mg}^{2+}(\text{aq})$	-2.37
$\text{Al(s)}/\text{Al}^{3+}(\text{aq})$	-1.66
$\text{Zn(s)}/\text{Zn}^{2+}(\text{aq})$	-0.76
$\text{Fe(s)}/\text{Fe}^{2+}(\text{aq})$	-0.45
$\frac{1}{2}\text{H}_2(\text{g})/\text{H}^+(\text{aq})$	0.00
$\text{Cu(s)}/\text{Cu}^{2+}(\text{aq})$	+0.34
$\text{I}^-(\text{aq})/\frac{1}{2}\text{I}_2(\text{aq})$	+0.54
$\text{Ag(s)}/\text{Ag}^+(\text{aq})$	+0.80
$\text{Br}^-(\text{aq})/\frac{1}{2}\text{Br}_2(\text{aq})$	+1.09
$\text{Cl}^-(\text{aq})/\frac{1}{2}\text{Cl}_2(\text{aq})$	+1.36
$\text{F}^-(\text{aq})/\frac{1}{2}\text{F}_2(\text{aq})$	+2.87



# HL Spontaneity of electrochemical reactions

## SHORTHAND NOTATION FOR A CELL

To save drawing out the whole cell a shorthand notation has been adopted. A half-cell is denoted by a / between the metal and its ions, and two vertical lines are used to denote the salt bridge between the two half cells,

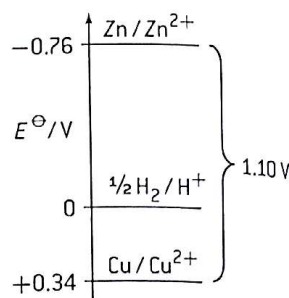
e.g.  $\text{Cu(s)}/\text{Cu}^{2+}(\text{aq}) \parallel \text{H}^+(\text{aq})/\text{H}_2(\text{g})$  and  
 $\text{Zn(s)}/\text{Zn}^{2+}(\text{aq}) \parallel \text{H}^+(\text{aq})/\text{H}_2(\text{g})$

The standard electromotive force (emf) of any cell  $E^\circ_{\text{cell}}$  is simply the difference between the standard electrode potentials of the two half-cells,

e.g.  $\text{Zn(s)}/\text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq})/\text{Cu(s)}$

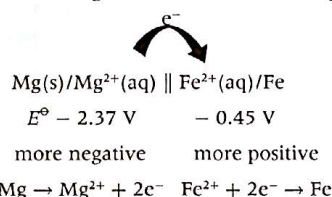
$$E^\circ -0.76 \text{ V} \quad +0.34 \text{ V}$$

$$E^\circ_{\text{cell}} = 1.10 \text{ V}$$



## ELECTRON FLOW, SPONTANEOUS REACTIONS AND FREE ENERGY

By using standard electrode potentials it is easy to see what will happen when two half-cells are connected together. The electrons will always flow from the more negative half-cell to the more positive half-cell, e.g. consider an iron half-cell connected to a magnesium half-cell:



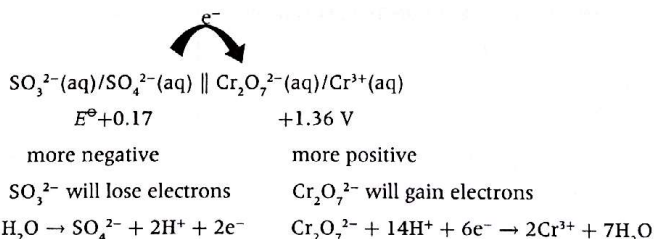
Spontaneous reaction:  $\text{Mg(s)} + \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{Fe(s)} \quad E^\circ_{\text{cell}} = 1.92 \text{ V}$

From the expression  $\Delta G^\circ = -nFE^\circ$  it can be seen that positive  $E^\circ_{\text{cell}}$  values give negative  $\Delta G^\circ$  values, which is obvious as the cell is producing electrical energy that can do work as the reaction is spontaneous. The actual amount of energy can be calculated as  $F$  is one Faraday and has a value equal to  $9.65 \times 10^4 \text{ C mol}^{-1}$  and  $1 \text{ Joule} = 1 \text{ Volt} \times 1 \text{ Coulomb}$ . The transfer of two mol of electrons is involved.  $\Delta G^\circ = -2 (\text{mol}) \times 9.65 \times 10^4 (\text{C mol}^{-1}) \times 1.92 (\text{V}) = -3.71 \times 10^5 \text{ J} = -371 \text{ kJ}$ .

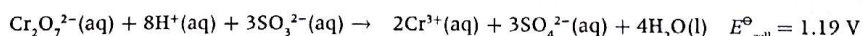
The reverse reaction ( $\text{Fe(s)} + \text{Mg}^{2+}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{Mg(s)}$ ) has a negative  $E^\circ_{\text{cell}}$  value which gives a positive value of  $+371 \text{ kJ}$  for  $\Delta G^\circ$  and the reaction will not be spontaneous. This reaction could only proceed if an external source of energy is provided greater than  $371 \text{ kJ}$ , i.e. a voltage greater than  $1.92 \text{ V}$  is supplied to force the reaction in the opposite direction. It is worth noting that just because a reaction is thermodynamically spontaneous (i.e. has a negative  $\Delta G^\circ$  value) it does not mean that it will necessarily proceed, as the reaction may have a large activation energy which first needs to be overcome.

## REDOX EQUATIONS

Standard electrode potentials can be extended to cover any half-equation. The values, which can be found in the Electrochemical Series in the IB data booklet, can then be used to determine whether a particular reaction is spontaneous. For example,  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})/\text{Cr}^{3+}(\text{aq})$ ,  $E^\circ = +1.36 \text{ V}$ , but this only takes place in acid solution, so hydrogen ions and water are required to balance the half-equation. Consider the reaction between acidified dichromate(VI) ions,  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ , and sulfite ions,  $\text{SO}_3^{2-}(\text{aq})$ . Using standard electrode potentials the cell becomes:

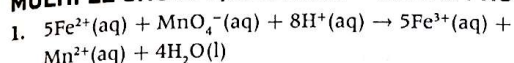


As previously explained, to obtain the overall equation the number of electrons in both half-equations must be equal. This is achieved by multiplying the sulfite equation by three. The two equations are then added together and the water and hydrogen ions, which appear on both sides, are simplified to give:



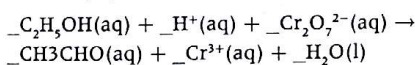
The acid that is normally added to supply the  $\text{H}^+(\text{aq})$  ions is sulfuric acid, since acidified dichromate ions cannot oxidize sulfate ions. The standard electrode potential for the  $\frac{1}{2}\text{Cl}_2(\text{aq})/\text{Cl}^-(\text{aq})$  half-cell is  $+1.36 \text{ V}$ . This is exactly the same as the value for the  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})/\text{Cr}^{3+}(\text{aq})$  half-cell. Under standard conditions dichromate ions will not oxidize chloride ions from hydrochloric acid to chlorine but the conditions only need to be changed slightly and this may no longer be true so hydrochloric acid should never be used to acidify the solution of dichromate ions.

## MULTIPLE CHOICE QUESTIONS – REDOX PROCESSES



In the equation above:

- $\text{Fe}^{2+}(\text{aq})$  is the oxidizing agent
  - $\text{H}^{+}(\text{aq})$  ions are reduced
  - $\text{Fe}^{2+}(\text{aq})$  ions are oxidized
  - $\text{MnO}_4^{-}(\text{aq})$  is the reducing agent
2. The oxidation states of nitrogen in  $\text{NH}_3$ ,  $\text{HNO}_3$  and  $\text{NO}_2$  are, respectively
- 3, -5, +4
  - +3, +5, +4
  - 3, +5, -4
  - 3, +5, +4
3. Which one of the following reactions is **not** a redox reaction?
- $\text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
  - $2\text{Na}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{NaCl}(\text{s})$
  - $\text{Mg}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2(\text{g})$
  - $\text{Cu}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Zn}^{2+}(\text{aq})$
4. Which substance does not have the correct formula?
- iron(III) sulfate  $\text{Fe}_2(\text{SO}_4)_3$
  - iron(II) oxide  $\text{Fe}_2\text{O}$
  - copper(I) sulfate  $\text{Cu}_2\text{SO}_4$
  - copper(II) nitrate  $\text{Cu}(\text{NO}_3)_2$
5. For which conversion is an oxidizing agent required?
- $2\text{H}^{+}(\text{aq}) \rightarrow \text{H}_2(\text{g})$
  - $2\text{Br}^{-}(\text{aq}) \rightarrow \text{Br}_2(\text{aq})$
  - $\text{SO}_3(\text{g}) \rightarrow \text{SO}_4^{2-}(\text{aq})$
  - $\text{MnO}_2(\text{s}) \rightarrow \text{Mn}^{2+}(\text{aq})$
6. Ethanol can be oxidized to ethanal by an acidic solution of dichromate(VI) ions.

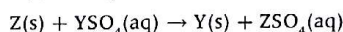
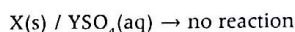


The sum of all the coefficients in the balanced equation is:

- 24
- 26
- 28
- 30

7. When an  $\text{Fe}(\text{s})/\text{Fe}^{2+}(\text{aq})$  half-cell is connected to a  $\text{Cu}(\text{s})/\text{Cu}^{2+}(\text{aq})$  half-cell by a salt bridge and a current allowed to flow between them
- the electrons will flow from the copper to the iron.
  - the salt bridge allows the flow of ions to complete the circuit.
  - the salt bridge allows the flow of electrons to complete the circuit.
  - the salt bridge can be made of copper or iron.
8. During the electrolysis of molten sodium chloride using platinum electrodes
- sodium is formed at the negative electrode.
  - chlorine is formed at the negative electrode.
  - sodium is formed at the positive electrode.
  - oxygen is formed at the positive electrode.
9. Which statement is true?
- Lead chloride is ionic so solid lead chloride will conduct electricity.
  - When a molten ionic compound conducts electricity free electrons pass through the liquid.
  - When liquid mercury conducts electricity mercury ions move towards the negative electrode.
  - During the electrolysis of a molten salt reduction will always occur at the negative electrode.

10. The following information is given about reactions involving the metals X, Y and Z and solutions of their sulfates.



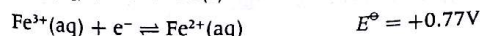
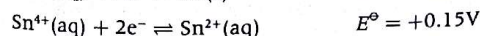
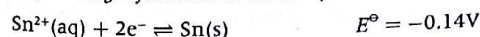
When the metals are listed in decreasing order of reactivity (most reactive first), what is the correct order?

- $\text{Z} > \text{Y} > \text{X}$
- $\text{X} > \text{Y} > \text{Z}$
- $\text{Y} > \text{X} > \text{Z}$
- $\text{Y} > \text{Z} > \text{X}$



11. Which are correct for a spontaneous reaction occurring in a voltaic cell?
- $E^{\circ}$  for the cell has a positive value
  - $\Delta G^{\circ}$  for the reaction has a negative value
  - The reaction must occur under standard conditions
- I and II only
  - I and III only
  - II and III only
  - I, II and III
12. When the same quantity of electricity was passed through a dilute solution of sodium hydroxide and through a molten solution of lead bromide, 0.100 mol of lead was produced. What amount (in mol) of hydrogen gas was evolved?
- 0.014
  - 0.050
  - 0.100
  - 0.200

Use the following information to answer questions 13 and 14.



13. Under standard conditions which statement is correct?
- $\text{Sn}^{2+}(\text{aq})$  can reduce  $\text{Fe}^{3+}(\text{aq})$ .
  - $\text{Fe}(\text{s})$  can oxidize  $\text{Sn}^{2+}(\text{aq})$ .
  - $\text{Sn}(\text{s})$  can reduce  $\text{Fe}(\text{s})$ .
  - $\text{Fe}^{3+}(\text{aq})$  can reduce  $\text{Sn}^{4+}(\text{aq})$ .
14. When a half-cell of  $\text{Fe}^{2+}(\text{aq})/\text{Fe}^{3+}(\text{aq})$  is connected by a salt bridge to a half-cell of  $\text{Sn}^{2+}(\text{aq})/\text{Sn}^{4+}(\text{aq})$  under standard conditions and a current allowed to flow in an external circuit the total emf of the spontaneous reaction will be:
- +0.92V
  - 0.92V
  - +0.62V
  - 0.62V



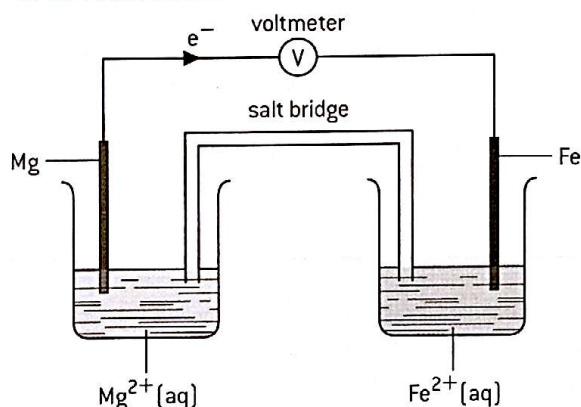
## SHORT ANSWER QUESTIONS – REDOX PROCESSES

1. The data below is from an experiment used to determine the percentage of iron present in a sample of iron ore. This sample was dissolved in acid and all of the iron was converted to  $\text{Fe}^{2+}$ . The resulting solution was titrated with a standard solution of potassium manganate(VII),  $\text{KMnO}_4$ . This procedure was carried out three times. In acidic solution,  $\text{MnO}_4^-$  reacts with  $\text{Fe}^{2+}$  ions to form  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  and the end point is indicated by a slight pink colour.

Titre	1	2	3
Initial burette reading / $\text{cm}^3$	1.00	23.60	10.00
Final burette reading / $\text{cm}^3$	24.60	46.10	32.50

Mass of iron ore / g	$3.682 \times 10^{-1}$
Concentration of $\text{KMnO}_4$ solution / $\text{mol dm}^{-3}$	$2.152 \times 10^{-2}$

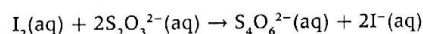
- Deduce the balanced redox equation for this reaction in **acidic** solution. [2]
  - Identify the reducing agent in the reaction. [1]
  - Calculate the amount, in moles, of  $\text{MnO}_4^-$  used in the titration. [2]
  - Calculate the amount, in moles, of Fe present in the  $3.682 \times 10^{-1}$  g sample of iron ore. [2]
  - Determine the percentage by mass of Fe present in the  $3.682 \times 10^{-1}$  g sample of iron ore. [2]
2. Chemical energy can be converted to electrical energy in the voltaic cell below.



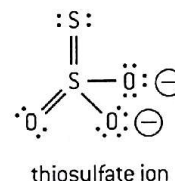
- Explain how the diagram confirms that magnesium is above iron in the activity series. [2]

- Identify the positive electrode (anode) of the cell. [1]
  - (i) State the half-equation for the reaction occurring at the iron electrode. [1]  
(ii) State the overall equation for the reaction when the cell is producing electricity. [2]
  - Deduce whether the voltage produced by the cell would be greater or less if the iron half-cell is replaced by a copper half-cell. [2]
3. a) Molten sodium chloride can be electrolysed using graphite electrodes.
- Draw the essential components of this electrolytic cell and identify the products that form at each electrode. [2]
  - State the half-equations for the oxidation and reduction processes and deduce the overall cell reaction, including state symbols. [2]
- b) Explain why solid sodium chloride does not conduct electricity. [1]
- c) Using another electrolysis reaction, aluminium can be extracted from its ore, bauxite, which contains  $\text{Al}_2\text{O}_3$ . State **one** reason why aluminium is often used instead of iron in many engineering applications. [1]

4. Iodine reacts with thiosulfate ions to form the tetrathionate ion according to the equation



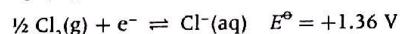
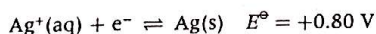
- Show that this reaction is a redox reaction. [2]
- The thiosulfate ion has a structure similar to the sulfate ion,  $\text{SO}_4^{2-}$ , except that one of the outer oxygen atoms has been replaced by a sulfur atom.



- Comment on the difference in the oxidation state of sulfur in the thiosulfate ion compared with the sulfate ion. [2]
  - Explore the concept of oxidation state using the tetrathionate ion,  $\text{S}_4\text{O}_6^{2-}$ , as an example. [3]
- c) Discuss whether the complete combustion of carbon in oxygen to form carbon dioxide can be described as the oxidation of carbon according to all the different definitions of oxidation. [4]



5. Consider the following two half-equations:



- Deduce the overall equation for the spontaneous reaction that will occur when a silver half-cell is connected to a chlorine half-cell. [2]
- Identify the direction of electron flow in the external circuit when the cell is operating. [1]
- Determine the cell potential,  $E^\ominus_{\text{cell}}$ . [1]
- Calculate the free energy produced by the cell when it is operating under standard conditions. [2]

- Identify the products that will be obtained at the positive (anode) and negative (cathode) electrodes when (i) a dilute solution and (ii) a concentrated solution of sodium chloride undergoes electrolysis. [3]
- Explain why the electrolysis of a dilute solution of sulfuric acid or a dilute solution of sodium hydroxide are both sometimes described as the electrolysis of water. [3]
- Describe how you could use electrolysis to coat a spoon made of steel with a thin layer of silver. [2]