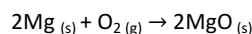


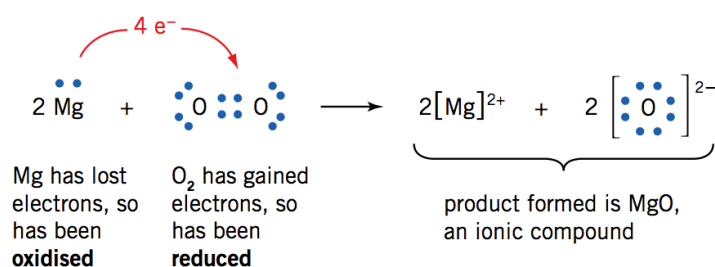
- We have considered chemical reactions involving the gain and loss of protons (i.e. acid-base reactions)
- We will now consider chemical reactions involving the gain and loss of electrons (i.e. reduction-oxidation or REDOX reactions)

## Reduction-Oxidation Reactions

- Let us consider the combustion of magnesium metal:



- If we consider the magnesium metal and oxygen gas separately, the above reaction can be split into two **half-reactions**
  - o  $\text{Mg} \rightarrow \text{Mg}^{2+}$ 
    - In order to balance the charges on either side of the equation, we must add 2 electrons to the right side
      - $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^{-}$
    - Thus it can be seen that magnesium metal has **lost 2 electrons**
  - o  $\text{O}_2 \rightarrow \text{O}^{2-}$ 
    - In order to balance the charges on either side of the equation, we must add 2 electrons to the left side
      - $\text{O}_2 + 2\text{e}^{-} \rightarrow \text{O}^{2-}$
    - Thus it can be seen that oxygen has **gained 2 electrons**
- There are no electrons present in the overall equation
  - o Therefore the only rational explanation is that magnesium has lost its two electrons to the hydrogen ions
- If a substance loses electrons, as the magnesium has, it is said to have been oxidised or to have undergone **oxidation**
- A substance that gains electrons in a reaction, like the  $\text{O}_2$  molecules, is said to have been reduced or to have undergone **reduction**



- A reaction in which one substance has been oxidised and another has been reduced is called a reduction-oxidation or **REDOX reaction**
- The two equations showing the loss of electrons (by Mg atoms) and the gain of electrons (by the  $\text{O}_2$  molecules) are called **half-equations**
- Remember the mnemonic: **OIL RIG**
  - o Oxidation Is Losing
  - o Reduction Is Gaining
- The reactant that causes the oxidation of another substance is called the **oxidant** or the **oxidising agent**
  - o In the process of removing electrons from the other reactant, the oxidant gains these electrons and so is reduced
  - o E.g. In the combustion reaction of magnesium, the magnesium is oxidised and so has acted as the reductant
- A **reductant** or **reducing agent** is a substance that causes another substance to undergo reduction
  - o This means a reductant gives electrons to another substance, and in this process the reductant is oxidised
  - o E.g. In the combustion reaction of magnesium, the oxygen has been reduced and so has acted as the oxidant

## Oxidation Number

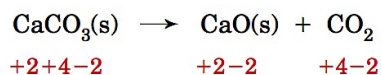
- In a reaction where a metal loses electrons or a non-metal gains electrons to form ions, it is easy to decide which substance has been reduced and which has been oxidised
  - o Similarly, when metal ions gain electrons or non-metal ions lose electrons, the REDOX nature is obvious
- However, there are many REDOX reactions in which the electron transfer process is not evident, particularly those reactions that involve the oxidation and reduction of substances with covalent bonds.
  - o E.g. When carbon is heated in the presence of oxygen, it burns to produce carbon dioxide:  
$$\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$$
    - The carbon has been oxidised in this reaction and, according to the definition of oxidation, must have 'lost electrons'
      - Some of the electrons that originally 'belonged' to the carbon are now being shared with oxygen atoms, but there has been no complete transfer
- To track the electron transfer process in such reactions, chemists have introduced the concept of oxidation number
  - o An oxidation number is a number that is assigned to each atom in a substance to indicate its oxidation state
- The rules for assigning oxidation numbers are as follows:
  - o The oxidation number of any element is zero. This also includes any element that is:
    - Monatomic (e.g. noble gases)
    - Composed of molecules or a covalent network substance (e.g. diamond)
  - o The oxidation number of an atom in a monatomic ion is the same as the charge on the ion
    - E.g.  $\text{Na}^+$  has an oxidation number of +1,
    - E.g.  $\text{O}^{2-}$  has an oxidation number of -2
  - o The oxidation number of oxygen in its compounds is -2
    - The exceptions to this rule are:
      - Fluorine oxide,  $\text{F}_2\text{O}$  where the oxygen has an oxidation number of +2
      - Peroxides ( $\text{O}_2^{2-}$ ), where the oxygen has an oxidation number -1
        - o E.g. In sodium peroxide,  $\text{Na}_2\text{O}_2$ , the oxidation number of oxygen is -1
  - o The oxidation number of hydrogen in its compounds is +1
    - The exception to this rule is the metal hydrides ( $\text{H}^-$ ), where the hydrogen has an oxidation number of -1
      - E.g. In lithium hydride,  $\text{LiH}$ , the oxidation number of hydrogen is -1
  - o The sum of the oxidation numbers of the atoms in a neutral compound is zero
    - E.g. The oxidation number of C in  $\text{CO}_2$  is +4 (as  $4 + 2(-2) = 0$ )
    - E.g. The oxidation number of N in  $\text{NH}_3$  is -3 (as  $-3 + 3(1) = 0$ )
    - E.g. The oxidation number of Na in  $\text{Na}_2\text{O}_2$  is +2 (as  $2(2) + 2(-2) = 0$ )
    - E.g. The oxidation number of Na in  $\text{NaH}$  is +1 (as  $1 + (-1) = 0$ )
  - o The sum of the oxidation numbers of the atoms in a polyatomic ion must equal the ionic charge
    - E.g. The oxidation number of S in  $\text{SO}_4^{2-}$  is +6 (as  $6 + 4(-2) = -2$ )
    - E.g. The oxidation number of P in  $\text{H}_2\text{PO}_4^-$  is +5 (as  $2(1) + 5 + 4(-2) = -1$ )
  - o An atom undergoes oxidation if its oxidation number increases during a chemical reaction
  - o An atom undergoes reduction if its oxidation number decreases during a chemical reaction
- **An atom undergoes oxidation if its oxidation number increases during a chemical reaction**
- **An atom undergoes reduction if its oxidation number decreases during a chemical reaction**

- Oxidation numbers can therefore be used to determine:

o Whether a reaction is REDOX or not

▪ Some reactions, including acid-base reactions and precipitation reactions, do not show a change in the oxidation numbers of the atoms, and so there is no REDOX process involved

• E.g. The decomposition of calcium carbonate: The oxidation number of each element has remained the same (and hence the reaction is not REDOX)

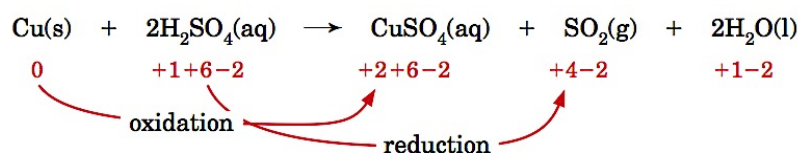


▪ E.g. The combustion of methane: The oxidation number of the elements has remained the same (and hence the reaction is REDOX)



o What species is oxidised or reduced in a REDOX reaction

▪ E.g. Copper metal reacting with concentrated sulfuric acid:



• For copper, Cu, its oxidation number has increased from 0 to +2. Thus copper has been oxidised, serving as the reductant

• For sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, the oxidation number of S has decreased from +6 to +4. Thus sulfuric acid has been reduced, serving as the oxidant

## REDOX Equations

- Simple REDOX equations (e.g. those involving metals and their ions), can be easily separated into their component oxidation and reduction half-equations

o E.g.  $\text{Cu}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$

▪ Oxidation half-equation:  $\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$

▪ Reduction half-equation:  $2\text{Ag}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Ag}(\text{s})$

o The electron transfer process is obvious in such reactions and so the identification of the individual oxidation and reduction half-equations and the overall ionic equation for the reaction is straightforward

- A more complex reaction, such as the reaction of an acidified solution of potassium dichromate, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, with a solution of sodium oxalate, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, to produce carbon dioxide and a solution of sodium ions, chromium (III) ions and potassium ions, is not as easy to represent by an overall ionic equation

- A series of simple rules allow the half-equations for more complex reactions in an acidic environment ( $H^+$ ) to be derived
  - o For each half-reaction:
    - Construct a 'skeleton equation' that identifies the atoms/molecules/ions undergoing the change in oxidation number
 
$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

$$C_2O_4^{2-} \rightarrow CO_2$$
    - Balance the atom undergoing the change in oxidation number
 
$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$$

$$C_2O_4^{2-} \rightarrow 2CO_2$$
    - Balance oxygen atoms by adding  $H_2O$ , where needed
 
$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

$$C_2O_4^{2-} \rightarrow 2CO_2$$
    - Balance hydrogen atoms by adding  $H^+$  where needed
 
$$14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

$$C_2O_4^{2-} \rightarrow 2CO_2$$
    - Balance the charge by adding electrons where needed
 
$$6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

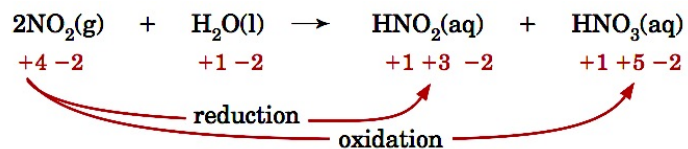
$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$
    - Multiply one or both of the half-reactions by an integer that will make the number of electrons lost in the oxidation half-equation equal the number of electrons gained in the reduction half-equation
 
$$6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

$$3C_2O_4^{2-} \rightarrow 6CO_2 + 6e^-$$
  - o Add the 2 half-reactions as if they were mathematical equations. The electrons will always cancel. If the same formulas are found on opposite sides of the half-reactions, you can cancel them. If the same formulas are found on the same side of both half-reactions, combine them
 
$$6e^- + 14H^+ + Cr_2O_7^{2-} + 3C_2O_4^{2-} \rightarrow 2Cr^{3+} + 7H_2O + 6CO_2 + 6e^-$$

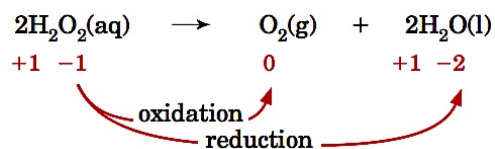
$$14H^+ + Cr_2O_7^{2-} + 3C_2O_4^{2-} \rightarrow 2Cr^{3+} + 7H_2O + 6CO_2$$
  - o Check to make sure that the atoms and the charges balance

### Disproportionation Reactions

- Reactions in which a single substance undergoes both oxidation and reduction, are called disproportionation reactions
- In the formation of acid rain, one of the oxides of nitrogen,  $\text{NO}_2$ , combines with water to produce a mixture of nitrous and nitric acid



- o This is an unusual reaction:
  - The oxidation number of nitrogen in nitrogen dioxide has:
    - Gone up from +4 to +5 in  $\text{HNO}_3$  (oxidation)
    - Gone down from +4 to +3 in  $\text{HNO}_2$  (reduction)
  - I.e. The nitrogen dioxide has been both oxidised and reduced
    - An alternative way of looking at it is that the nitrogen dioxide has acted as both the oxidant and the reductant
- Another example of a disproportionation reaction is the decomposition of hydrogen peroxide to produce oxygen and water:



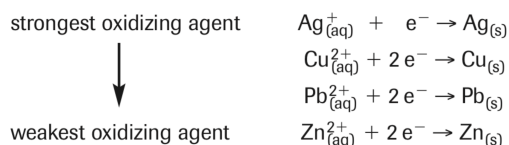
- o In this reaction the oxidation number of the oxygen atoms in  $\text{H}_2\text{O}_2$  has changed from -1 to 0 and -2. I.e. the  $\text{H}_2\text{O}_2$  has undergone both oxidation and reduction

### Development of a REDOX Table

- A REDOX reaction may be explained as a transfer of valence electrons from one substance to another. Since two particles must be involved in an electron transfer, this transfer can be explained as a competition for electrons. Using a tug-of-war analogy, each particle pulls on the same electrons
  - o If one particle is able to pull electrons away from the other, a spontaneous reaction occurs
  - o Otherwise, no reaction occurs
- Without mixing all possible reactants and observing any evidence of reaction, how can we predict if a reaction will occur? If a reaction occurs, what will be the products? By observing many successful and unsuccessful reactions, patterns emerge and empirical generalisations can be made
- Some REDOX reactions such as single displacement reactions are easy to study experimentally. Let's look at some examples of combinations of metals and metal ions. Suppose copper, lead, silver, and zinc metals were combined one at a time with each of copper(II), lead(II), silver, and zinc ion solutions
  - o We can rank the ability of the metal ions to react with the metals:

Ions	$\text{Ag}^+_{(\text{aq})}$	$\text{Cu}^{2+}_{(\text{aq})}$	$\text{Pb}^{2+}_{(\text{aq})}$	$\text{Zn}^{2+}_{(\text{aq})}$
Reacted with	$\text{Cu}_{(\text{s})}, \text{Pb}_{(\text{s})}, \text{Zn}_{(\text{s})}$	$\text{Pb}_{(\text{s})}, \text{Zn}_{(\text{s})}$	$\text{Zn}_{(\text{s})}$	none
Number of reactions	3	2	1	0
Reactivity order	most <span style="font-size: 2em;">→</span>			least

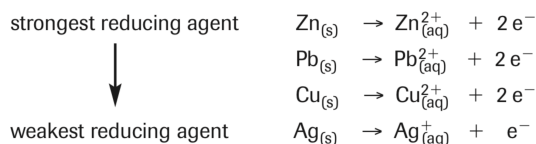
- The most reactive metal ion,  $\text{Ag}^+_{(\text{aq})}$ , has the greatest tendency to gain electrons. Meanwhile,  $\text{Zn}^{2+}_{(\text{aq})}$  shows no tendency to gain electrons in the combinations tested. Therefore, the order of reactivity is also the order of strengths as oxidising agents



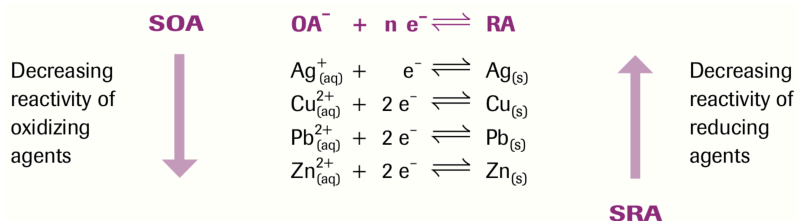
- o The order of reactivity of the four metals can be obtained in a similar way:

Metals	$\text{Zn}_{(\text{s})}$	$\text{Pb}_{(\text{s})}$	$\text{Cu}_{(\text{s})}$	$\text{Ag}_{(\text{s})}$
Reacted with	$\text{Ag}^+_{(\text{aq})}, \text{Cu}^{2+}_{(\text{aq})}, \text{Pb}^{2+}_{(\text{aq})}$	$\text{Ag}^+_{(\text{aq})}, \text{Cu}^{2+}_{(\text{aq})}$	$\text{Ag}^+_{(\text{aq})}$	none
Number of reactions	3	2	1	0
Reactivity order	most <span style="font-size: 2em;">→</span>			least

- The most reactive metal,  $\text{Zn}_{(\text{s})}$ , has the greatest tendency to lose electrons and  $\text{Ag}_{(\text{s})}$  shows no tendency to lose electrons in the combinations tested. Metals behave as reducing agents and so  $\text{Zn}_{(\text{s})}$  is the strongest reducing agent among those tested

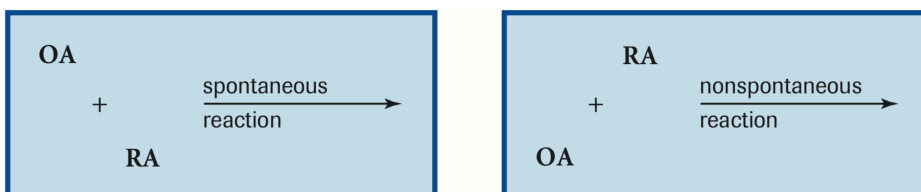


- In these reactions, the metal ions are the oxidising agents and the silver ion is the strongest oxidising agent (SOA) of the four ions because it is the most reactive in our group. The metals are the reducing agents and the zinc metal is the strongest reducing agent (SRA). The two lists of reactivity can be summarized using a single set of half reactions as



shown below:

- The metal ions are on the left side of the equations and the metal atoms are on the right side. For metal ions (the oxidising agents), the half-reaction equations are read from left to right in the table. For metal atoms (the reducing agents), the half-reaction equations are read from right to left
- Evidence obtained from the study of many REDOX reactions has been used to establish a generalisation, called the REDOX spontaneity rule
  - A spontaneous REDOX reaction occurs only if the oxidising agent (OA) is above the reducing agent (RA) in a table of relative strengths of oxidising and reducing agents



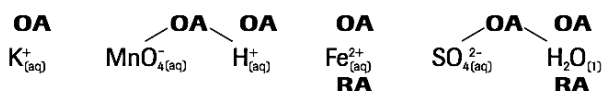
- Evidence collected in many experiments has been analysed to produce an extended REDOX table of oxidising and reducing agents such as the one found on the Data Sheet

## Predicting REDOX Reactions

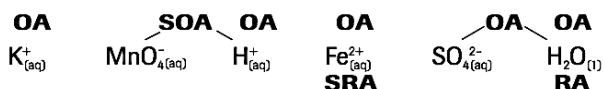
- The steps in predicting REDOX reactions are as follows:
  - o List all entities that are present and classify them as oxidising or reducing agents. Note the following points:
    - Aqueous solutions contain  $\text{H}_2\text{O}_{(l)}$  molecules
    - Acidic solutions contain  $\text{H}^+_{(aq)}$  ions
    - Basic solutions contain  $\text{OH}^-_{(aq)}$  ions
    - Some oxidising and reducing agents are combinations, for example,  $\text{MnO}_4^-_{(aq)}$  and  $\text{H}^+_{(aq)}$
    - Many substances may act as either oxidising or reducing agents. Label both possibilities
  - o Choose the strongest oxidising agent present in the mixture by starting at the top left corner of the REDOX table and going down the list until you find the oxidising agent that is in the mixture
  - o Choose the strongest reducing agent in the mixture by starting at the bottom right corner of the REDOX table and going up the list until you find the reducing agent that is in the mixture
  - o Reduction half-reaction equations are read from left to right (following the forward arrow)
  - o Oxidation half-reaction equations are read from right to left (following the reverse arrow)
  - o Any substances not present in the REDOX table will be assumed to be spectator ions. These do not need to be considered

- E.g. Suppose a solution of potassium permanganate is slowly poured into an acidified iron(II) sulfate solution. Identify the REDOX reaction that occurs

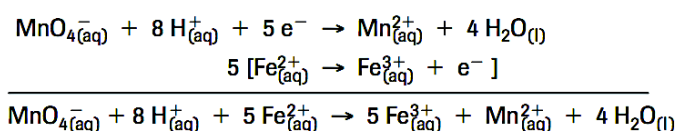
- o The entities present are copper atoms, potassium ions, permanganate ions, hydrogen ions and water molecules



- The permanganate ion is listed as an oxidising agent only in an acidic solution. To indicate this combination, draw an arc between the permanganate and hydrogen ions as shown, and label the pair as an oxidising agent
- o The standard reduction potential table is used to choose the strongest oxidising agent and the strongest reducing agent from the list and indicate them with SOA and SRA



- o The skeleton half-equations are written the balance, and the complete REDOX reaction is written



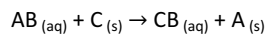


## Displacement Reactions

**- Metal Displacement Reactions**

- A metal displacement reaction occurs when a metal is added to an ionic solution containing the ion of another metal. The anion in this solution is just a spectator ion

- The general equation for a metal displacement reaction is written as:

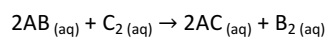


- This exemplifies that the metal C has displaced the ions of metal A out of solution

**- Halogen Displacement Reactions**

- A halogen displacement reaction occurs when a halogen is added to an ionic solution containing the ion of another halogen (i.e. a halide solution). The cation in this solution is just a spectator ion

- The general equation for a halogen displacement reaction is written as:



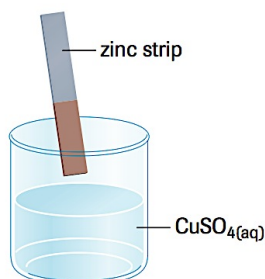
- This exemplifies that the halogen  $C_2$  has displaced the halide ions  $B^-$  out of solution

## REDOX Titrations

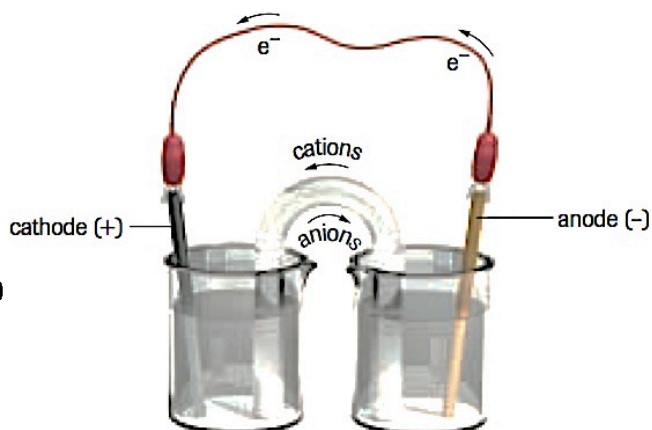
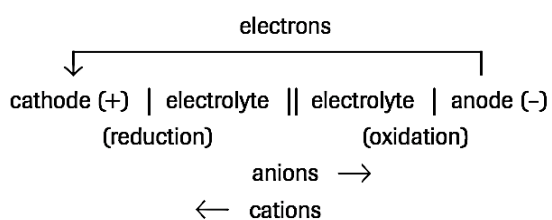
- The same procedures are involved in REDOX titrations as in acids and bases, except that the reactions involve oxidation and reduction
- Commonly used:
  - o Oxidising agents include:
    - Potassium permanganate (acidified):  $\text{KMnO}_4$   
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
    - Potassium dichromate (acidified):  $\text{K}_2\text{Cr}_2\text{O}_7$   
 $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
    - Hydrogen peroxide (acidified):  $\text{H}_2\text{O}_2$   
 $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$
    - Iodine:  $\text{I}_2$   
 $\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$
  - o Reducing agents include:
    - Oxalic acid:  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$   
 $\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$
    - Ammonium iron (II) sulfate:  $(\text{NH}_4)_2 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$   
 $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$
    - Sodium oxalate:  $\text{Na}_2\text{C}_2\text{O}_4$   
 $\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2\text{e}^-$
    - Hydrogen peroxide:  $\text{H}_2\text{O}_2$   
 $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$
- Potassium permanganate ( $\text{KMnO}_4$ )
  - o  $\text{KMnO}_4$  is a strong oxidising agent and is commonly used for REDOX titrations
  - o  $\text{KMnO}_4$  acts as a self-indicator (i.e. it changes colour at the end of the titration)
    - The product of its reduction  $\text{Mn}^{2+}$  is nearly colourless, being a very faint pink
    - During a titration with  $\text{KMnO}_4$  the purple colour of  $\text{MnO}_4^-$  is removed as soon as it is added because it is reduced to  $\text{Mn}^{2+}$ . As soon as the titration is complete, a fraction of a drop of excess  $\text{MnO}_4^-$  solution imparts a definite pink colour to the solution, indicating that reaction is complete
  - o  $\text{KMnO}_4$  cannot be used a primary standard due to the presence of impurities such as  $\text{MnO}_2$

## Electrochemical/Galvanic Cells

- Consider the spontaneous reaction of copper(II) ions and zinc metal, the  $\text{Cu}^{2+}$  ion is electron deficient and pulls electrons from a Zn atom:  $\text{Zn}_{(s)} + \text{Cu}^{2+}_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{Cu}_{(s)}$

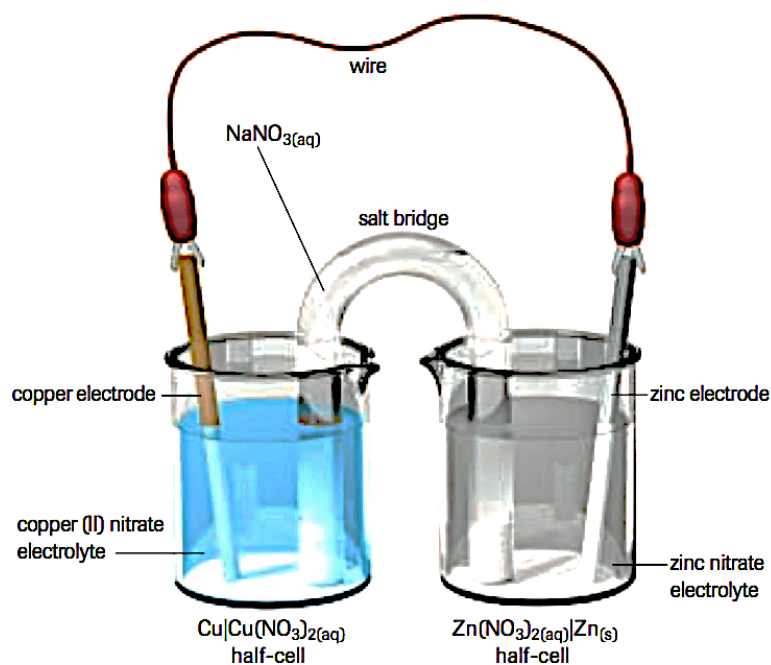


- o The reaction occurs spontaneously because  $\text{Cu}^{2+}$  is a stronger oxidising agent than  $\text{Zn}^{2+}$  (and because of course Zn is a stronger reducing agent than Cu)
- In the current experiment set-up, the REDOX reaction produces simply heat energy as the transfer of electrons is direct. In order to utilise the energy of the exothermic REDOX reaction as electrical energy it is necessary to construct an electrochemical or galvanic cell
- The design of an electrochemical cell “plays a trick” on oxidising and reducing agents, resulting in electrons passing through an external circuit (i.e. indirectly) rather than directly from one substance to another
  - o This cell transfers the electrons through a wire (known as the external circuit) from the reductant to the oxidant, rather than allowing the reactants to come into direct contact with one another
  - o The two pieces of metal in the separate beakers are called electrodes
  - o The two solutions that the electrode is placed into to facilitate current flow are called electrolytes
  - o The electrode at which oxidation occurs is called the anode and the electrode at which reduction occurs is called the cathode



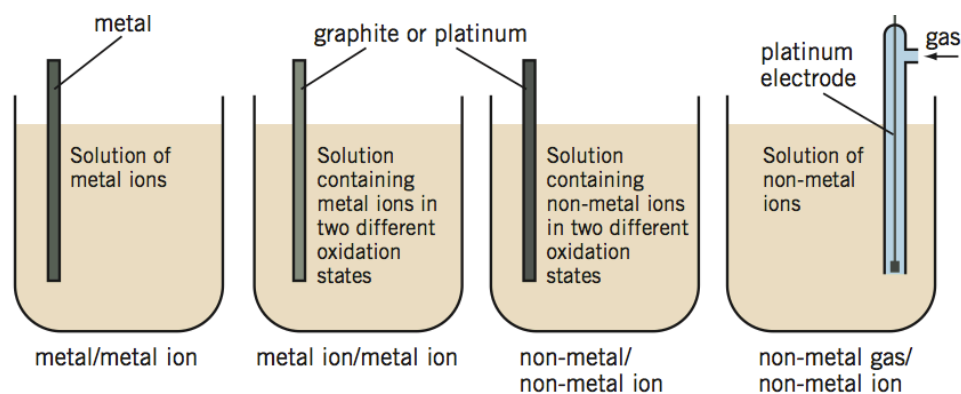
- Remember the mnemonic: **AN OIL RIG CAT**
  - o Anode: Oxidation Is Losing
  - o Cathode: Reduction Is Gaining

- To complete the circuit, a **salt bridge** joins the two beakers
  - The salt bridge contains an electrolyte solution, usually a saturated solution of a salt such as potassium nitrate whose ions will not react with the contents of either of the beakers
  - The salt bridge allows for the flow of positive and negative ions to maintain electrolyte neutrality
- The electrochemical cell that converts chemical potential energy of the reacting copper and zinc ions into electrical energy is shown below



- The two beakers and contents that make up the electrochemical cell are called half-cells
  - The beaker containing the zinc electrode is the half-cell in which oxidation takes place
  - The beaker containing the copper electrode is the half-cell in which the reduction takes place
- These half-reactions are:
  - Oxidation half-cell reaction (at the anode):  $\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}_{(aq)} + 2e^{-}$
  - Reduction half-cell reaction (at the cathode):  $\text{Cu}^{2+}_{(aq)} + 2e^{-} \rightarrow \text{Cu}_{(s)}$
- The electrons that are produced at the negative anode move through the wire of the external circuit to the positive cathode
- As a result of these two half-reactions:
  - The mass of the zinc electrode will decrease while that of the copper electrode will increase
  - The concentration of zinc ions in the oxidation half-cell will increase, and the concentration of copper ions in the reduction half-cell will decrease

- REDOX reactions are not limited to those between metals and metal ions. As a result, it is necessary to construct half-cells that can accommodate other types of reactions if electrical energy is to be obtained from these reactions



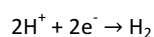
- Reactions that involve a **metal** and a **metal ion**
  - The metal becomes the electrode and it is placed in a solution containing its ions
  - E.g. Copper metal placed in a solution of copper(II) ions
- Reactions that involve **metal ions in different oxidation states**
  - A graphite or platinum is placed in a solution containing both of the metal ions
  - E.g. Graphite electrode placed in a solution containing iron(III) and iron(II) ions
- Reactions that involve a **dissolved non-metal** and **its ions**
  - A graphite or platinum is placed in a solution containing both the non-metal and its ions
  - E.g. A platinum electrode placed in a solution containing bromine and dissolved bromide ions
- Reactions that involve a **gaseous non-metal** and **its ions**
  - The gas is bubbled over a platinum electrode immersed in a solution of the non-metal ions
  - E.g. Hydrogen gas bubbling over a surface of platinum placed in a solution containing hydrogen ions

## Standard Cells and Potentials

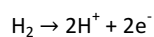
- As established earlier, different oxidants have different strengths
  - $F_2$  is a strong oxidant
  - $Na^+$  is a very weak oxidant
- It therefore follows that if a half-cell containing a strong oxidant is connected to a half-cell containing a weak oxidant, the electrons in the external circuit wire will be 'pulled' towards the half-cell with the stronger oxidant
- A measure of the electron-attracting 'power' of an oxidant in a half-cell is referred to as the **reduction potential** of the half-cell
- The 'driving force' causing the flow of electricity in an electrochemical cell is due to the difference in reduction potentials of its two half-cells. This driving force or 'pull' of electrons in an electrochemical cell is called the cell potential or potential difference of the cell
  - The unit of measurement of the cell potential is Volts (V)
- The cell potential of an electrochemical cell not only depends on the nature of the oxidants and reductants in each half-cell, but also depends on the concentrations of the electrolytes, the pressure of any gases involved in the reaction and the temperature at which the cell operates
  - When the conditions in a cell are  $1 \text{ mol L}^{-1}$  concentration of dissolved substances and at STP (i.e. 100.0 kPa pressure of gases and  $25^\circ\text{C}$ ) the cell potential of the cell is called the standard cell potential

## Standard Hydrogen Half-Cell

- It is impossible to determine experimentally the reduction potential of a single half-cell because electron transfer requires both an oxidising agent and a reducing agent
  - I.e. The voltmeter can only measure a potential difference
- In order to assign values for standard reduction potentials, we measure the "reducing" strength of all possible half-cells relative to an accepted standard half-cell
- The value of a standard electrode potential is referred to as the  $E^\circ$  value
  - Note the technical difference between the terms standard electrode potential and standard reduction potential
    - The standard electrode potential is that of either the reduction or oxidation equation
    - The standard reduction potential is that of only the reduction equation
- The half-cell used for this purpose is the standard hydrogen half-cell and is arbitrarily assigned an electrode/reduction potential of exactly zero volts

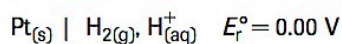
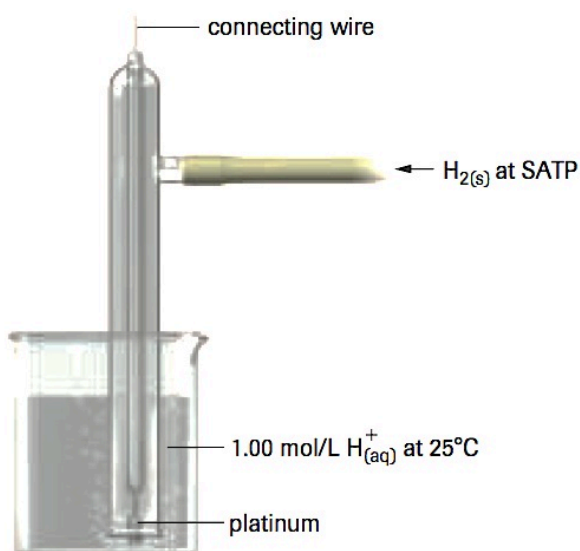


$$E^\circ_{\text{reduction}} = 0.00 \text{ V}$$



$$E^\circ_{\text{oxidation}} = 0.00 \text{ V}$$

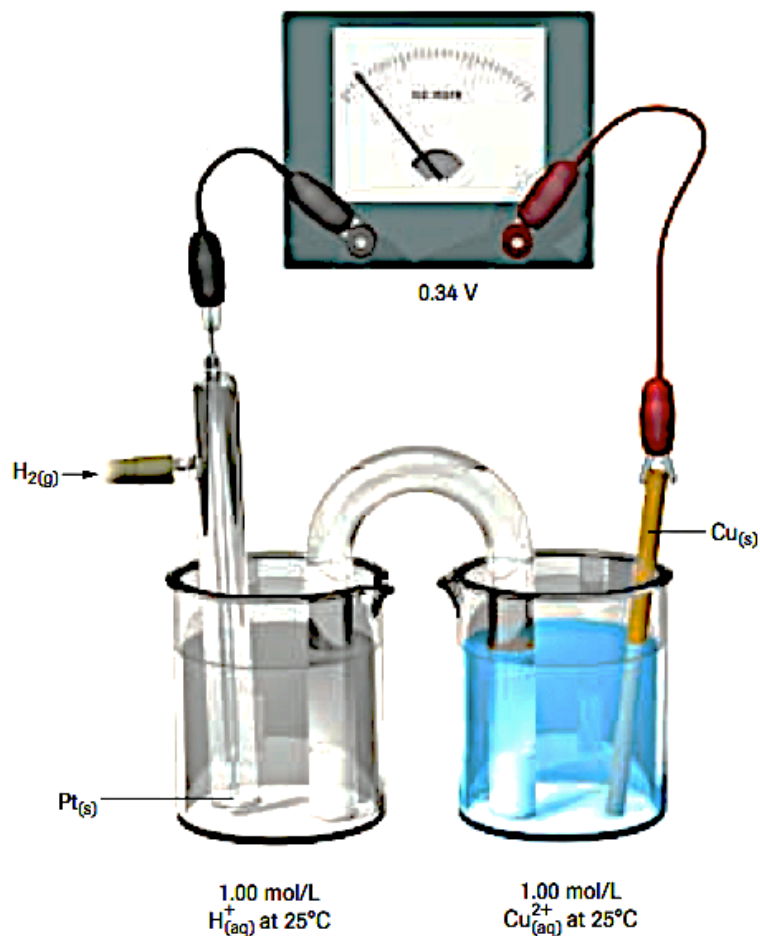
- The standard hydrogen half-cell consists of an inert platinum electrode immersed in a  $1.00 \text{ mol L}^{-1}$  solution of hydrogen ions with the pressure and temperature of the cell are kept at STP conditions



- Standard electrode potentials for all half-cells are measured relative to that of the standard hydrogen half-cell
  - o As a result, a numerical value can be assigned to the potential associated with every other reaction
  - o When a half-reaction, written as a reduction equation, has a positive potential, we conclude that the oxidising agent in that half-reaction is a stronger oxidising agent than the hydrogen ion
    - This implies that the oxidising agent will be reduced spontaneously
    - Therefore, if this half-cell was connected to a standard hydrogen half-cell, electrons would be drawn away from the standard hydrogen electrode
  - o When a half-reaction, written as a reduction equation, has a negative potential, we conclude that the hydrogen ion is a stronger oxidising agent than the oxidising agent in that half-reaction
    - This implies that the oxidising agent will not be reduced spontaneously. Instead the reverse reaction will occur
    - Therefore, if this half-cell was connected to a standard hydrogen half-cell, electrons would be drawn towards the standard hydrogen electrode
- The standard cell potential can be calculated using the standard electrode potentials of both the oxidant and reductant in the following way:
 
$$E_{cell}^\circ = E_{reduction}^\circ (\text{cathode}) + E_{oxidation}^\circ (\text{anode})$$

$$= E_{reduction}^\circ (\text{cathode}) - E_{reduction}^\circ (\text{anode})$$
  - o Note that changing the stoichiometric coefficients in any half-cell equation (to balance the number of electrons) does not alter the value of the standard reduction potential for that half-cell
  - o Note that the Data Sheet only provides standard reduction potential values (for reduction equations). Thus the standard oxidation potential (for oxidation equations) must have the sign of the associated reduction equation reversed
- This formula exemplifies that a positive cell potential indicates that the net reaction is spontaneous, a requirement for all electrochemical cells
  - o This is consistent with our knowledge that a spontaneous REDOX reaction occurs only if the oxidising agent is above the reducing agent in a standard reduction potential table

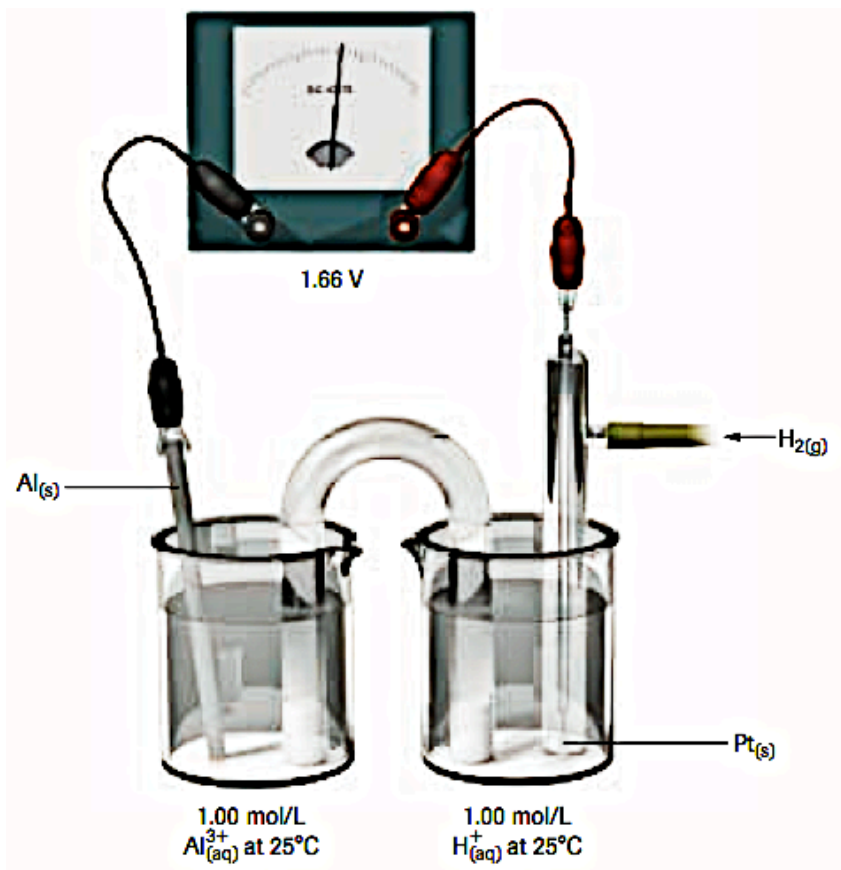
- The cell formed between the half-cells  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{H}_2/\text{H}^+$  is shown below:



- The voltmeter shows that the standard cell potential of the above configuration is 0.34 V
  - o This experimental value could have been theoretically confirmed with knowledge of the standard electrode potentials of both individual half-cells
    - $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$  (cathode)  $E^\circ_{\text{reduction}} = 0.34 \text{ V}$
    - $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$  (anode)  $E^\circ_{\text{oxidation}} = 0.00 \text{ V}$
  - o  $E^\circ_{\text{cell}} = 0.34 + 0.00 = 0.34 \text{ V}$
- We know the above reaction occurs (i.e. copper(II) ions are being reduced to copper metal and hydrogen molecules are being oxidised to hydrogen ions), because if the voltmeter is replaced by a connecting wire so that the current is allowed to flow:
  - o The blue colour of the copper(II) ion disappears (i.e.  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ )
  - o The pH of the hydrogen half-cell decreases (i.e.  $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ )



- The cell formed between the half-cells  $\text{Al}/\text{Al}^{3+}$  and  $\text{H}^+/\text{H}_2$  is shown below:



- The voltmeter shows that the standard cell potential of the above configuration is 1.66 V
  - o This experimental value could have been theoretically confirmed with knowledge of the standard electrode potentials of both individual half-cells
    - $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  (cathode)       $E^\circ_{\text{reduction}} = 0.00 \text{ V}$
    - $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$  (anode)       $E^\circ_{\text{oxidation}} = 1.66 \text{ V}$
  - o  $E^\circ_{\text{cell}} = 0.00 + 1.66 = 1.66 \text{ V}$
- We know the above reaction occurs (i.e. hydrogen ions are being reduced to hydrogen gas and aluminium metal is being oxidised to aluminium ions) occurs, because If the voltmeter is replaced by a connecting wire so that the current is allowed to flow:
  - o The pH of the hydrogen half-cell increases, and a colourless, odourless gas is evolved (i.e.  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ )
  - o The mass of the aluminium electrode decreases, and the solution remains colourless (i.e.  $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$ )
- The cell potential illustrates the extent to which a reaction is to proceed in the direction predicted
  - o The greater the difference in  $E^\circ$  values, the larger the equilibrium constant for the reaction
  - o The cell potential does not illustrate any details regarding the rate of reaction

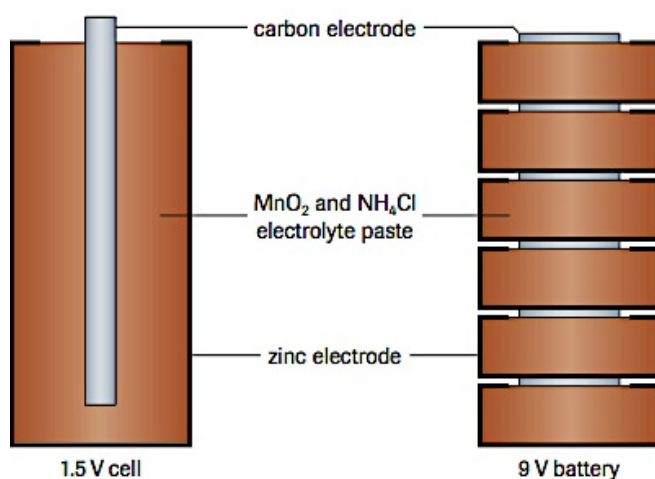
- An aspect of REDOX reactions that is not highlighted by the table of standard reduction potentials relates to the fact that water behaves as an oxidant and a reductant in a neutral solution
  - o While the reduction and oxidation half-equations remain the same, the values of the reduction potentials change
    - $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$   $E^\circ = 0.82 \text{ V}$
    - $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$   $E^\circ = -0.41 \text{ V}$
  - o This is because the concentration of  $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  is  $10^{-7} \text{ mol L}^{-1}$  and not  $1 \text{ mol L}^{-1}$ . The reduction table however, as we know, only provides  $E^\circ$  values for standard conditions
  - o However, for this course of study the differences in these values from those in the table of standard reduction potentials will not be important
- Standard reduction potentials can be used to explain reactions such as:
  - o Metal displacement reactions
  - o Halogen displacement reactions
  - o Reactions of metals with water: Any metal with a reduction potential less than around  $-0.4 \text{ V}$  will react with water
  - o Reactions of metals with acids
    - Metals with a reduction potential less than  $0.0 \text{ V}$  will react with hydrochloric acid and dilute sulfuric acid to form  $\text{H}_2$
    - Most metals will react with concentrated nitric acid to form nitrogen dioxide gas  
 $\text{NO}_3^+(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
    - Most metals will react with concentrated sulfuric acid to form sulfur dioxide gas  
 $\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

### Commercial Electrochemical Cells

- A cell or a battery is an electrochemical cell that stores useful energy in the form of an oxidant and a reductant that are capable of releasing energy when required
- While any redox reaction could be harnessed as an energy source for a cell, in practice there are certain limitations, such as cost, portability and lifetime, which restrict the choice of materials
- The three major types of cells are:
  - o Primary cells
  - o Secondary cells
  - o Fuel cells:

#### Primary Cells

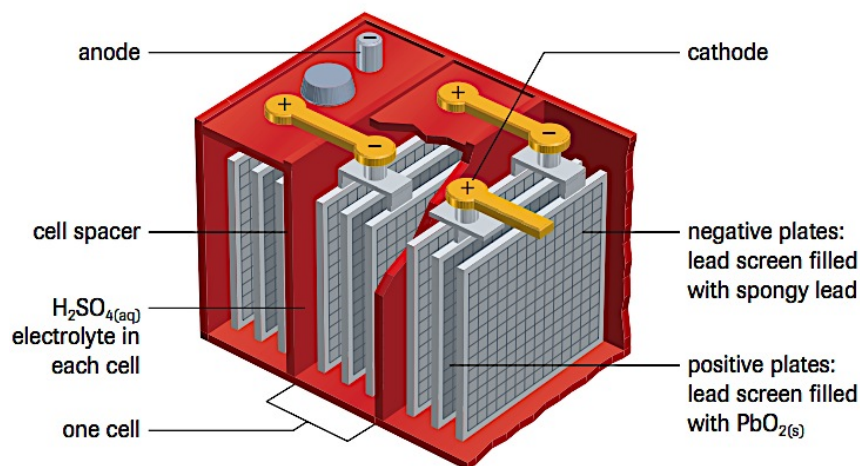
- Primary cells contain a fixed amount of oxidant and reductant, which once consumed, cannot be replaced/regenerating by any process of recharging to reverse the reaction
- The most familiar primary cell is the **dry cell** (Leclanché cell)



- o The dry cell consists of:
  - An outer casing of zinc (anode)
  - A graphite rod (cathode) surrounded by a paste of MnO<sub>2</sub>
  - An electrolyte paste of MnO<sub>2</sub>, NH<sub>4</sub>Cl and ZnCl<sub>2</sub> (electrolyte)
- o The electrode reactions are:
  - Anode:  $\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}_{(aq)} + 2e^{-}$
  - Cathode:  $2\text{MnO}_{2(s)} + 2\text{NH}_4^{+}_{(aq)} + 2e^{-} \rightarrow \text{Mn}_2\text{O}_3(s) + 2\text{NH}_3(aq) + \text{H}_2\text{O}(l)$
- o The dry cell produces a cell potential (voltage) of around 1.5 V

### Secondary Cells

- Secondary cells can be recharged by using electricity to recharge/reverse the chemical reaction that occurs spontaneously when the cell discharges
- The most familiar secondary cell is the **lead-acid accumulator**, which is widely used in motor vehicles

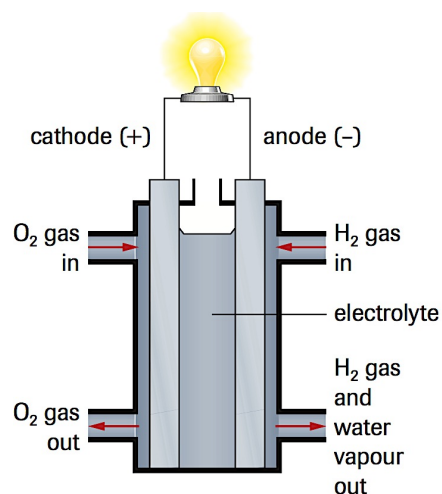


- o The lead acid accumulator consists of:
  - Electrodes:
    - Anode:
      - o Finely divided spongy lead
      - o  $\text{Pb}_{(s)} + \text{SO}_4^{2-}{}_{(aq)} \rightarrow \text{PbSO}_4(s) + 2e^-$
    - Cathode:
      - o Lead (IV) oxide placed packed on metal grid
      - o  $\text{PbO}_2(s) + \text{SO}_4^{2-}{}_{(aq)} + 4\text{H}^+{}_{(aq)} + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$
  - An electrolyte of concentrated sulfuric acid
- o The lead acid accumulator produces a cell potential of around 2 V. A typical car battery consists of 6 cells placed in series (producing a total potential of 12 V)
- o The half reactions above give us the overall discharge reaction (i.e. when the battery is being used) of:
 
$$\text{Pb}_{(s)} + \text{PbO}_2(s) + 4\text{H}^+{}_{(aq)} + 2\text{SO}_4^{2-}{}_{(aq)} \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$$
  - Lead sulfate is formed at each electrode, and this forms a coating on the electrodes
  - Sulfuric acid is consumed in the cathode reaction and so the acid becomes less concentrated. Because of this, the electrolyte becomes less dense since a solution of sulfuric acid has a higher density than water
    - Thus measuring the density of the electrolyte can be used to check the extent to which the battery has been discharged

- In the recharging process, electrical energy is converted into chemical energy
  - If an external voltage that is larger than the cell potential is applied to the cell, the electrode reactions can be reversed with  $\text{PbSO}_4$  being reduced to  $\text{Pb}$  at one electrode and oxidised to  $\text{PbO}_2$  at the other
  - The lead electrode is connected to the negative terminal of the charging power source, and the lead(IV) oxide electrode is connected to the positive terminal of the charging power source (i.e. the anode and cathode reactions are reversed)
  - The cell reaction that occurs during the recharging or charging process is the reverse to the reaction that occurs spontaneously during discharging:
 
$$2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq})$$

## Fuel Cells

- While recharging can regenerate the oxidants and reductants in secondary cells, it is also possible to produce a cell in which the reactants are supplied continuously to (and the products expelled continuously from) the electrodes
  - Such a cell is called a fuel cell (which is different to both primary or secondary cells)
- The most common fuel cell is based on the reaction between hydrogen and oxygen to form water in the **hydrogen-oxygen fuel cell**



- The hydrogen-oxygen fuel cell consists of:
  - Compressed electrodes of porous platinum or graphite
  - Electrolyte that is either acidic (e.g.  $\text{HCl}$ ) or basic (e.g.  $\text{KOH}$ )
  - Anode: Hydrogen gas
    - Acid electrolyte:  $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$
    - Alkaline electrolyte:  $\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^-$
  - Cathode: Oxygen gas
    - Acid electrolyte:  $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$
    - Alkaline electrolyte:  $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$
- The overall reaction (for both acid or alkaline electrolytes) is:  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$

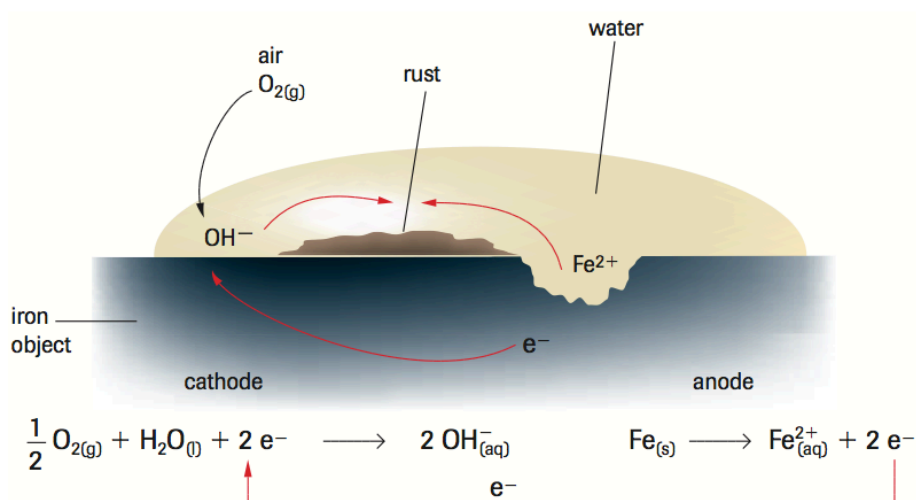
## Corrosion of Metals

- Corrosion is an electrochemical process that occurs when metals are oxidised by substances in their environment
  - o Anode (metal oxidises):  $\text{Metal} \rightarrow (\text{Metal ions})^{x+} + x e^{-}$
  - o Cathode: 4 common reduction procedures are given below:
    - $2\text{H}^{+} + 2e^{-} \rightarrow \text{H}_2$ 
      - Metal exposed to moisture and acidic conditions
    - $\text{O}_2 + 2\text{H}_2\text{O} + 4e^{-} \rightarrow 4\text{OH}^{-}$ 
      - Metal exposed to moisture and oxygen (very common)
    - $2\text{H}_2\text{O} + 2e^{-} \rightarrow \text{H}_2 + 2\text{OH}^{-}$ 
      - Metal exposed to moisture but a low concentration of oxygen (e.g. shovel blade in soil)
    - $(\text{Metal ions})^{x+} + x e^{-} \rightarrow \text{Metal}$ 
      - Metal in contact with another metal with a greater reduction potential
- When some metals oxidise, they form a rough, protective oxide-coating that greatly limits the ability of the oxidising agent to come in contact with the metal
  - o E.g. Aluminium. Even though aluminium will oxidise rapidly, the oxide coating protects the underlying aluminium from further corrosion
  - o E.g. Iron. Iron forms an iron coating that is easily penetrated by water and oxygen, and subsequently the oxide layer does not protect the iron from further corrosion

**Rust: A Special Case of Corrosion**

- The most common example of corrosion is the oxidation of iron
  - o Anode: Areas of stress in the iron become anodic
  - o Cathode: Areas of high oxygen concentration become cathodic
  - o Electrons flow from the metal from the anode to the cathode
  - o Electrolyte: The moisture acts as an electrolyte

- The formation of rust involves a series of reactions:
  - o The initial oxidation of the iron:
    - Anode:  $\text{Fe}_{(s)} \rightarrow \text{Fe}^{2+}_{(aq)} + 2e^{-}$
    - Cathode:  $\text{O}_{2(g)} + 2\text{H}_2\text{O}_{(l)} + 4e^{-} \rightarrow 4\text{OH}^{-}_{(aq)}$ 
      - The cathode may be an impurity, such as carbon, in the iron, or a region of high oxygen concentration
    - The iron(II) ions and the hydroxide ions produced diffuse towards each other and precipitate as iron(II) hydroxide, according to the following equation:
      - $\text{Fe}^{2+}_{(aq)} + 2\text{OH}^{-}_{(aq)} \rightarrow \text{Fe}(\text{OH})_{2(s)}$



- o The further oxidation of the  $\text{Fe}(\text{OH})_{2(s)}$  formed
    - $\text{Fe}(\text{OH})_{2(s)} + \text{OH}^{-}_{(aq)} \rightarrow \text{Fe}(\text{OH})_{3(s)} + e^{-}$
    - $\text{Fe}(\text{OH})_{2(s)} + 2\text{H}_2\text{O}_{(l)} + \text{O}_{2(g)} \rightarrow 4\text{Fe}(\text{OH})_{3(s)}$
  - o The partial dehydration of the  $\text{Fe}(\text{OH})_{3(s)}$  to rust
    - $2\text{Fe}(\text{OH})_{3(s)} \rightarrow \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}_{(s)} + 2\text{H}_2\text{O}_{(l)}$
- Therefore, the overall equation for the process of rusting is:
 
$$4\text{Fe}_{(s)} + 3\text{O}_{2(g)} + 2\text{H}_2\text{O}_{(l)} \rightarrow 2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}_{(s)}$$

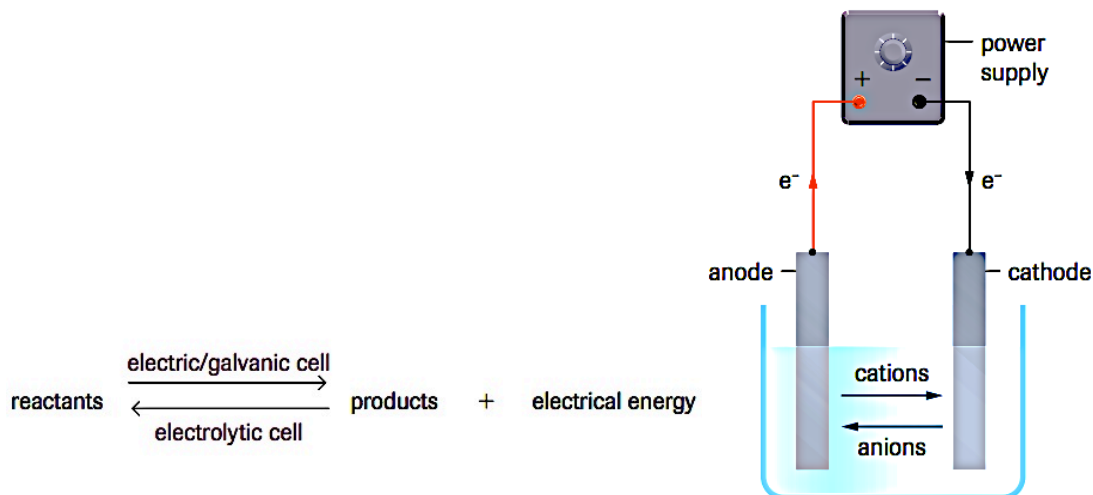
## Prevention of Corrosion

- The formation of rust on iron and steel can be slowed down or stopped by a number of methods
  - o **Application of a Surface Layer:** This is the coating of the iron with a non-metal or a less reactive metal
    - This will prevent oxygen and water from coming in contact with the iron
    - E.g. Paint, plastic, oil, tin, chromium or silver
      - If a less reactive metal is used as the coating, then any scratch on the iron's surface will lead to an accelerated rate of corrosion of the iron
        - o E.g. An iron can coated with tin. If the tin coating is scratched, the iron will become the anode (and will oxidise quicker than a piece of uncoated iron would), because the iron acts as the sacrificial anode
        - o This increase in corrosion rate of iron also occurs in any situation where the piece of iron is in contact with any other metal less active than itself
  - o **Galvanising:** This is the coating of the iron with a more reactive metal
    - The more reactive metal is sacrificially oxidised instead of the iron being oxidized. I.e. an electrochemical cell is created in which the more reactive metal acts as the anode, and the iron the cathode
    - E.g. An iron can coated with zinc. The more reactive zinc will give up its electrons, even if the surface coating is scratched
  - o **Sacrificial Anode:** This involves connecting the iron by a conducting wire to a more reactive metal
    - The method is very similar to galvanising, except that the reactive metal can be replaced easily after it has been consumed
  - o **Cathodic Protection:** This involves applying a voltage to make the iron negatively charged, thereby prevents its oxidation by making it the cathode of the electrochemical cell
    - This arrangement consists of the iron cathode, a DC power source and an anode
    - The anode can be made of:
      - Scrap metal, which must be replaced once consumed. The scrap metal is oxidised
      - An inert metal. The surrounding environment is oxidised



## Electrolytic Cells

- In electrolysis, an external power supply acts as an “electron pump”. The electric energy is used to do work on the electrons to cause an electron transfer inside the electrolytic cell from the anode to the cathode



- E.g. Consider what happens when lead electrodes are placed in a solution of zinc sulfate and the electrodes are connected with a wire
  - o There is no evidence of any reaction
  - o The strongest oxidising agent present is  $\text{Zn}^{2+}_{(\text{aq})}$  and the strongest reducing agent present is  $\text{Pb}_{(\text{s})}$ 
    - A reduction potential table shows that the oxidising agent is well below the position of the reducing agent
    - Thus the  $E^\circ$  of the only reaction that could occur is negative (note that the reverse reaction would be spontaneous but cannot occur because neither  $\text{Pb}^{2+}_{(\text{aq})}$  nor  $\text{Zn}_{(\text{s})}$  is present initially)
      - $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$  (cathode)  $E^\circ = -0.76 \text{ V}$
      - $\text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}^-$  (anode)  $E^\circ = 0.13 \text{ V}$
    - $E^\circ(\text{cell}) = -0.76 + 0.13 = -0.64 \text{ V}$
  - o This cell would not produce electricity because the reaction is nonspontaneous. However, by supplying electrical energy to a nonspontaneous cell, we can force the reaction to occur. This process is called electrolysis
  - o In this case, to force the cell reactions, electrons must be supplied with a minimum of 0.64 V from an external battery or other power supply. In practice, however, a greater voltage is required.

- In an electrolytic cell, the chemical reaction is the reverse of that of a spontaneous electrochemical/galvanic cell. However, most of the scientific principles already studied also apply to electrolytic cell, as highlighted by the table below

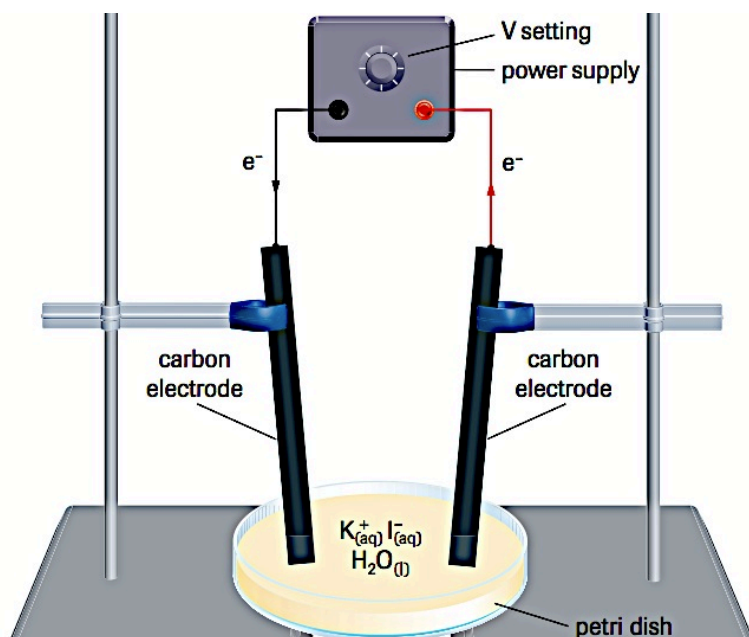
	Electrochemical Cell	Electrolytic Cell
<b>Spontaneity</b>	Spontaneous reaction	Nonspontaneous reaction
<b>Standard cell potential (i.e. <math>E^\circ</math>)</b>	Positive	Negative
<b>Cathode</b>	Strongest oxidising agent present undergoes reduction Positive electrode	Strongest oxidising agent present undergoes reduction Negative electrode
<b>Anode</b>	Strongest reducing agent present undergoes oxidation Negative electrode	Strongest reducing agent present undergoes oxidation Positive electrode
<b>Direction of electron flow</b>	Anode $\rightarrow$ Cathode	Anode $\rightarrow$ Cathode
<b>Direction of ion movement</b>	Anions $\rightarrow$ anode Cations $\rightarrow$ cathode	Anions $\rightarrow$ anode Cations $\rightarrow$ cathode

- Electrolytic cells have industrial applications that include:
  - o Extraction of elements
  - o Refining of metals
  - o Electroplating metals

### Extraction of Metals (Electrowinning)

- Most metals occur naturally combined with other elements in compounds. E.g. Ionic compounds of sodium, potassium, lithium, magnesium, calcium, and aluminum are abundant, but these reactive metals are not found uncombined in nature. This is because the reduction potentials for these metals are very negative, hence they are easily oxidised by practically all other substances

- E.g. Consider the observations when carbon electrodes are placed in a solution of potassium iodide, and an external voltage applied



- Litmus paper does not change colour in the initial solution and turns blue only near the electrode from which gas bubbles
    - At the other electrode, a yellow-brown colour and a dark precipitate forms. The yellow-brown substance produces a violet colour in a halogen test
  - The chemical evidence agrees with the interpretation supplied by the following half-reaction equations
 

OA		SOA
$K^+_{(aq)}$	$I^-_{(aq)}$	$H_2O_{(l)}$
	SRA	

    - $2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$
    - $2I^-_{(aq)} \rightarrow I_{2(s)} + 2e^-$
  - Evidence from the study of this and many other aqueous electrolytic cells confirms that the generalisations for electrochemical cells also apply to electrolytic cells
    - The strongest oxidising agent present in a particular mixture has the greatest attraction for electrons and gains electrons at the cathode
    - The strongest reducing agent present in the mixture has the least attraction for electrons and loses electrons at the anode
    - This demonstrates that the reaction that is most likely to occur is the one that requires the least input of energy (i.e. the least negative voltage)
- The conditions of an electrolytic cell are manipulated to favour specific reactions. The three factors that can be manipulated relate to the:
    - Nature of the electrolyte
    - Concentration of the electrolyte and the voltage used
    - Nature of the electrode

## Nature of the Electrolyte

- Many metals are produced by electrolysis of solutions of their ionic compounds. However, two difficulties arise for a numbering of metals:
  - o Many naturally occurring ionic compounds have a low solubility in water
  - o Water is a stronger oxidising agent than active metal cations
- To overcome these difficulties, a design in which water is not present can be used (i.e. the ionic compound is melted)
  - o The use of molten ionic compounds is possible as they are good electrical conductors and hence can function as the electrolyte in a cell
  - o In the electrolysis of molten binary ionic compounds, only one oxidising agent and one reducing agent are present (i.e. there is no need to consider whether water will preferentially be reduced or oxidised)
- E.g. Production of Strontium
  - o Strontium chloride is melted in an electrolytic cell with inert electrodes. In this cell, there are only two kinds of ions present,  $\text{Sr}^{2+}$  and  $\text{Cl}^-$
  - o As there are no other competing substances in the cell:
    - The strontium ions (i.e. SOA) will consume electrons at the cathode to form strontium metal  

$$\text{Sr}^{2+}_{(l)} + 2\text{e}^- \rightarrow \text{Sr}_{(s)}$$
    - The chloride ions (i.e. SRA) will give up electrons at the anode to form chlorine gas  

$$2\text{Cl}^-_{(l)} \rightarrow \text{Cl}_{2(g)} + 2\text{e}^-$$
  - o Electrons are balanced and adding the two equations gives the overall reaction in the cell  

$$\text{Sr}^{2+}_{(l)} + 2\text{Cl}^-_{(l)} \rightarrow \text{Sr}_{(s)} + \text{Cl}_{2(g)}$$
  - o This reaction would not be possible in an aqueous solution because water is a stronger oxidising agent than strontium ions
- Electrolysis of molten ionic compounds can be expensive because:
  - o A significant quantity of energy must be used
  - o The electrolysis cell must be specially designed to withstand the high temperatures involved
- A common method to reduce the temperature is to add an inert compound to the electrolyte form a mixture that melts at a lower temperature. In general, the melting point of any substance is lowered by adding an impurity
- E.g. Production of Sodium: Down's Cell
  - o Pure sodium chloride has a melting point of about  $800^\circ\text{C}$ , but when mixed with calcium chloride, the melting point is about  $600^\circ\text{C}$
  - o At the anode, the only reaction is the oxidation of chloride ions to form chlorine:  $2\text{Cl}^-_{(l)} \rightarrow \text{Cl}_{2(g)} + 2\text{e}^-$
  - o The key reaction at the cathode is the reduction of sodium ions to form sodium:  $\text{Na}^+_{(l)} + \text{e}^- \rightarrow \text{Na}_{(l)}$ 
    - In such a cell, the potential difference that is applied to the mixture must be controlled to reduce sodium ions but not calcium ions
- E.g. Production of Aluminium: Hall-Héroult Cell
  - o Initial efforts to produce aluminum by electrolysis were unproductive as no material could be found to hold the molten compound, because its ore  $\text{Al}_2\text{O}_3$ , had a high melting point of over  $2000^\circ\text{C}$
  - o Two scientists working independently (Hall and Héroult) discovered that  $\text{Al}_2\text{O}_3$  dissolved in a molten mineral called cryolite  $\text{Na}_3\text{AlF}_6$ . The cryolite acted as an inert solvent for the electrolysis of aluminum oxide, forming a molten conducting mixture with a melting point around  $1000^\circ\text{C}$
  - o Aluminum could then be produced electrolytically from this molten mixture

**Concentration of the Electrolyte and the Voltage Used**

- In the electrolysis of aqueous solutions, there are competitive reaction at both the anode and cathode
  - o The reaction that occurs at each electrode is the one that has the lowest negative voltage (i.e. the strongest oxidising agent reacts with the strongest reducing agent)
  - o However, where the  $E^\circ$  values for the competitive reactions are very similar, the concentration of the solution may need to be considered
- E.g. Electrolysis of copper chloride
  - o At the cathode, there is a large difference between the  $E^\circ$  values for the reduction of  $\text{Cu}^{2+}$  ions and the reduction of  $\text{H}_2\text{O}$ . Thus the concentration of the solution will not affect the preferred reaction for this electrode, and so the reduction of  $\text{Cu}^{2+}$  (i.e. the strongest oxidising agent) will occur
  - o At the anode, there is only a very small difference between the  $E^\circ$  values for the oxidation of  $\text{Cl}^-$  ions and the oxidation of  $\text{H}_2\text{O}$ . This implies that the concentration of the solution affects the preferred reaction for this electrode
    - In a more concentrated solution, there are more chloride ions in the same volume of solution. Therefore it is more likely that the chloride ions will be oxidised
    - However in a more dilute concentration, there are fewer chloride ions in the same volume of solution and thus is less likely that the chloride ions will be oxidised and more likely that the water is oxidised
- Another design that overcomes the difficulty of producing active metals by simply "overpowering" the reduction of the water. A high voltage leads to the reduction of metal ions rather than water because the reduction of water is a relatively slow reaction
- E.g. Aqueous sodium chloride is electrolysed using high voltages
  - o This forces, despite the relative positions of the species involved on the reduction potential table, the preferential:
    - Reduction of aqueous sodium ions to sodium metal at the cathode:  $\text{Na}^+_{(\text{aq})} + \text{e}^- \rightarrow \text{Na}_{(\text{s})}$
    - Oxidation of aqueous chloride ions to chlorine at the anode:  $2\text{Cl}^-_{(\text{aq})} \rightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^-$
  - o The sodium metal is then reacted with water to spontaneously produce hydrogen gas and sodium hydroxide

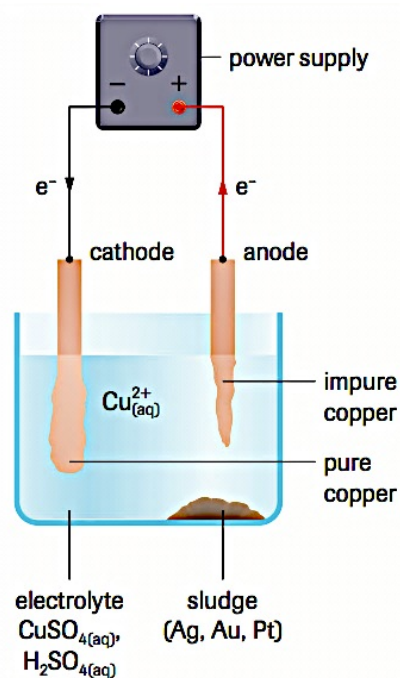
## Refining of Metals (Electrorefining)

- In the production of metals, the initial product is usually an impure metal. Impurities are often other metals that come from various compounds in the original ore

### Nature of the Electrode

- Electrorefining uses an electrolytic cell to obtain high-grade metals at the cathode from an impure metal at the anode
- Electrorefining differs from electrowinning because the refining process involves the oxidation of the anode (i.e. the anode is not inert as it is in the electrowinning process)
  - o While the use of electrodes made of graphite or unreactive metals such as platinum ensures that only those species present in the electrolyte undergo oxidation or reduction, where a more reactive metal is used as the positive electrode, it is possible for the electrode to be oxidised in preference to any other reductant in the cell
- E.g. Electrorefining of Copper
  - o The initial smelting process that produces copper that is about 99% pure, containing some silver, gold, platinum, iron, and zinc. The presence of even small amounts of other metal impurities can diminish its attributes (i.e. resistance to corrosion and high electrical conductivity). Following electrorefining, copper with a purity greater of 99.95% can be obtained
  - o Consider the electrolytic cell to the right:

- Anode: A slab of impure crude copper
- Cathode: A thin sheet of very pure copper
- Electrolyte: Copper(II) sulfate dissolved in sulfuric acid
- Copper and other reactive metals in the anode are oxidised
  - $\text{Cu}_{(s)} \rightarrow \text{Cu}^{2+}_{(aq)} + 2e^{-}$
  - $\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}_{(aq)} + 2e^{-}$
  - $\text{Fe}_{(s)} \rightarrow \text{Fe}^{2+}_{(aq)} + 2e^{-}$
- Only copper is reduced at the cathode (i.e.  $\text{Cu}^{2+}_{(aq)} + 2e^{-} \rightarrow \text{Cu}_{(s)}$ ), because:
  - There is a high concentration of copper ions in the electrolyte
  - The copper ion is a stronger oxidant than the ions of the more reactive metals
- Keeping the voltage suitably low prevents the oxidation of the silver, gold and platinum. Instead these less reactive metals fall to the bottom of the cell and form the anode sludge/slime



### Electroplating Metals

- Several metals, such as silver, gold, zinc, and chromium, are valuable because of their appearance and resistance to corrosion
  - o Unfortunately, products made from these metals in their pure form:
    - Are too expensive
    - Lack suitable mechanical properties (e.g. strength, hardness, etc)
  - o In order to achieve the best compromise among appearance, corrosion resistance, price and mechanical properties, items may be made of a relatively inexpensive, yet strong/hard, alloys such as steel, and then coated (plated) with another metal or alloy to improve appearance or corrosion resistance
  - o A common technique employed to coat one metal with another is called electroplating. Here, the metal to be coated is placed at the cathode, and the metal used as the coating is placed at the anode of an electrolytic cell

- E.g. Electroplating with Silver:

- o A layer of silver can be deposited onto another metal object by making that object the cathode in an electrolytic cell
- o Consider the electrolytic cell to the right:
  - Anode: A piece of pure silver
  - Cathode: The metal to be coated (e.g. a stainless steel spoon)
  - Electrolyte: A solution that contains silver ions
- o The electrode reactions for this cell are:
  - Anode reaction:  $\text{Ag}_{(s)} \rightarrow \text{Ag}^+_{(aq)} + e^-$
  - Cathode reaction:  $\text{Ag}^+_{(aq)} + e^- \rightarrow \text{Ag}_{(s)}$

