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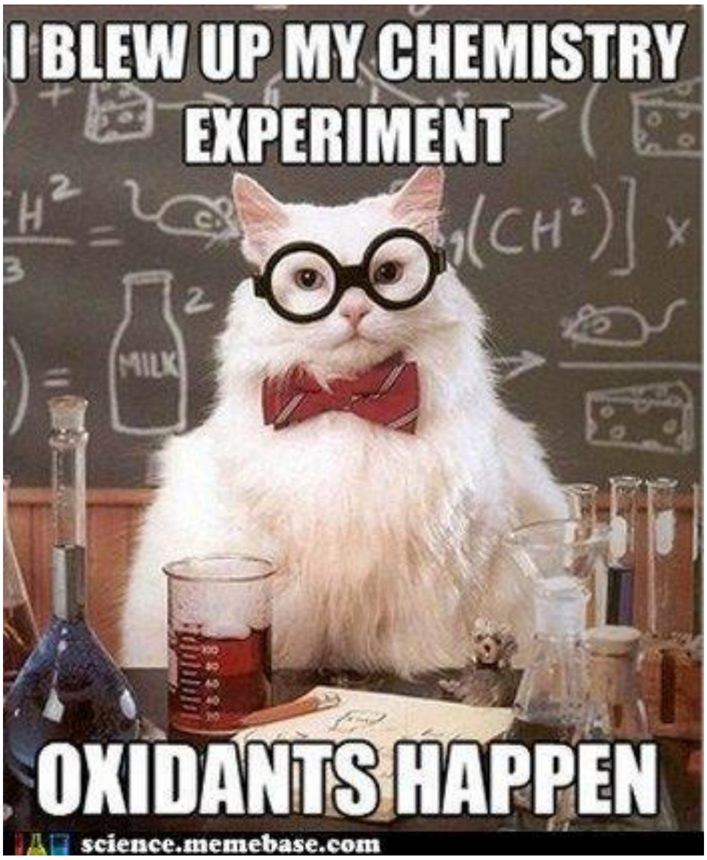
Redox Reactions



Unit 2 – Redox (Electron transfer) reactions

AOS 1 – Oxidising and reducing properties, writing half equations.

Applications of redox reactions

KEY KNOWLEDGE

Redox (electron transfer) reactions in water

- oxidising and reducing agents, conjugate redox pairs and redox reactions including writing of balanced half and overall redox equations with states indicated
- the reactivity series of metals and metal displacement reactions including balanced redox equations with states indicated
- the causes and effects of a selected issue related to redox chemistry

REDOX REACTIONS

Reactions that undergo oxidation or reduction are called redox reactions. These can include:

- Oxidation of food in our bodies
- Battery reaction
- Photosynthesis
- Combustion, explosions

Early definition

Oxidation – Combining with oxygen/ Addition of oxygen

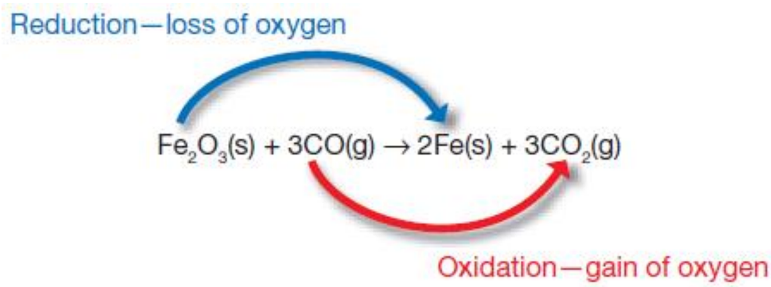
- i.e. Combustion reactions
  - $4Fe\ (s) + 3O_2\ (g) \rightarrow 2Fe_2O_3\ (s)$
  - Metals are exposed to the atmosphere and react with gases and water to form mineral ores

Reduction – Loss of Oxygen

- i.e. extraction of metal from iron ore
- $Fe_2O_3\ (s) + 3CO\ (g) \rightarrow 2Fe\ (l) + 3CO_2\ (g)$

However, this is only true for reactions involving oxygen.

The processes of oxidation and reduction always occur simultaneously.



Electron Transfer

The current view of redox reactions now includes many other reactions including combustion.

e.g. $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

Here magnesium has lost two electrons: $Mg(s) \rightarrow Mg^{2+}(s) + 2e^-$

The definition now involves electron transfer.

Oxidation – Electron Transfer

Oxidation is defined as the loss of ***electrons***. The substance that is oxidised loses electrons and is therefore an electron donor.

$$Mg(s) \rightarrow Mg^{2+}(s) + 2e^{-}$$

Reduction – Electron Transfer

Reduction is defined as the gain of ***electrons.*** The substance that is reduced is one that gains electrons and is therefore an electron acceptor.

$$O_2(g) + 4e^{-} \rightarrow 2O^{2-}(s)$$

Sample Problem 1

Explain why the following reaction is described as a redox reaction and identify the species oxidised and reduced.

$$\mathbf{Fe\,(s) + 2Ag^{+}\,(aq) \rightarrow 2Ag\,(s) + Fe^{2+}\,(aq)}$$

THINK	WRITE
1. Redox reactions are electron transfer reactions. To decide if electrons have been transferred, compare reactants and products and identify the changes.	$Fe(s)$ has become $Fe^{2+}(aq)$. $Ag^{+}(aq)$ has become $Ag(s)$.
2. Identify which reactant has lost electrons and which reactant has gained electrons. The species that has lost electrons is oxidised.	Fe has lost two electrons to become Fe^{2+}. Ag^{+} has gained an electron to become Ag. Fe is oxidised
The species that has gained electrons is reduced. TIP When naming ions, it is important to refer to them as ions and not just state the metal. In this case, the silver **ion** is reduced.	Ag^{+} is reduced; that is, the silver ion is reduced.
3. Electron transfer has occurred.	This is a redox reaction because electron transfer has occurred from Fe to Ag^{+}

PRACTICE PROBLEM 1

Explain why the following reaction is described as a redox reaction and identify the species oxidised and reduced.

$$\mathbf{Cl_2\,(aq) + 2Br^{-}\,(aq) \rightarrow Br_2\,(aq) + 2Cl^{-}\,(aq)}$$

Sample Problem 2

For the following reaction, write the:

a. ionic equation
b. half-equation
c. conjugate pairs.

$$2NaBr\,(aq) + Cl_2\,(g) \rightarrow 2NaCl\,(aq) + Br_2\,(l)$$

THINK	WRITE
a. 1. Show all ions and other species present in the full equation.	$2Na^+(aq) + 2Br^-(aq) + Cl_2(g) \rightarrow$ $2Na^+(aq) + 2Cl^-(aq) + Br_2(l)$
2. Write the ionic equation, omitting spectator ions (in this case, Na^+).	$2Br^-(aq) + Cl_2(g) \rightarrow 2Cl^-(aq) + Br_2(l)$
b. 1. Write the half-equation for the first reactant, *balancing the charges* by adding electrons to the appropriate side.	$2Br^-(aq) \rightarrow Br_2(l) + 2e^-$
2. Write the half-equation for the second reactant, *balancing the charges* by adding electrons to the appropriate side.	$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$
c. Identify the conjugate pairs from each equation.	$Br_2(l)/Br^-(aq)$ $Cl_2(g)/Cl^-(aq)$

PRACTICE PROBLEM 2

For the following equation, write the:

a. ionic equation
b. half-equation
c. conjugate pairs.

$$2AgNO_3\,(aq) + Cu\,(s) \rightarrow Cu(NO_3)_2\,(aq) + 2Ag\,(s)$$

OIL RIG

Oxidation Is Loss of electrons

Reduction Is Gain of electrons

WRITING HALF EQUATIONS

A half equation is an equation specifically written for the oxidation OR the reduction reaction. Electrons are shown in the equation to balance the charges on either side of the equation. Electrons don't have states

Example 1

When sodium metal reacts with chlorine gas (Cl_2), sodium chloride (an ionic compound containing Na^+ ions and Cl^- ions) is formed. The formation of ions can be represented by two half equations. Write their equations and identify the substances oxidised and reduced.

Example 2

When a strip of copper wire is suspended in a solution of silver ions, long crystals of silver metal can be observed. The solution changes to a pale blue colour, indicating the presence of Cu^{2+} (aq) ions.
Write half equations for this reaction and identify the substances oxidised and reduced.

Example 3

Write the oxidation and reduction half-equations for the reaction with the overall equation:

$$2Li\ (s) + Br_2\ (l) \rightarrow 2LiBr\ (s)$$

Overall Redox Equations

In order to write a full equation it is usual to write the two half equations first and then add them to get an overall equation. The overall equation should not show any electrons. The electrons lost in the oxidation reaction are gained in the reduction equation and therefore cancel out. Often you will need to balance the number of electrons.

Example 4

When sodium is oxidised by atmospheric oxygen, the reaction can be represented by the following half equations:

$$Na\ (s) \rightarrow Na^{+}\ (s) + e^{-}$$

$$O_2\ (g) + 4e^{-} \rightarrow 2O^{2-}\ (s)$$

Identify the half equation representing the oxidation reaction and write the balanced overall equation.

Example 5

Potassium metal is oxidised by oxygen gas in air to form solid potassium oxide. Write the half-equations for the reaction and hence write the balanced overall equation.

1. Balance the Key element
2. Balance a change in Oxygen by adding H_2O on the other side
3. Balance the Hydrogen in H_2O by adding H^+ ions to the other side
4. Balance the total charge on each side by adding Electrons
5. Add the States into the final, balanced equation (electrons do not have states)

Sample Problem 3

Write the half-equation for the reduction of permanganate ions, MnO_4^-(aq), to manganese ions, Mn^{2+}(aq).

THINK	WRITE
1. To balance the key element, state the conjugate pair and write it as a skeleton equation, then balance the equation, except for oxygen and hydrogen, which will be balanced next.	MnO_4^-(aq)/Mn^{2+}(aq) $MnO_4^- \rightarrow Mn^{2+}$ Manganese atoms are already balanced.
2. Balance oxygen atoms, where needed, by adding water.	$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
3. Balance hydrogen atoms, where needed, by adding H+.	$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
4. Equalise the charge of each half-equation by adding electrons. The total charge on the left is –1 + 8 = +7. On the right side, the total charge is +2. So, five electrons must be added to the left side. TIP Take care when balancing electrons	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
5. Add states; these reactions generally occur in aqueous solutions so the states are usually aqueous but be aware of common gases (g) and water, which is (l).	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+} + 4H_2O(l)$

Example: Balance the two half equations and then write the full redox equation

Fe^{2+} (aq) → Fe^{3+} (aq)

MnO_4^- (aq) → Mn^{2+} (aq)

Then combine both half equations for the overall redox reaction

Example: Potassium dichromate ($K_2Cr_2O_7$) reacts with potassium iodide (KI) in acidified solution. The dichromate ion ($Cr_2O_7^{2-}$) is reduced to form Cr^{3+}, and the iodide ion (I^-) is oxidised to I_2. Write:

- *The half equation for the oxidation of the I^- to I_2*
- *The half equation for the reduction of $Cr_2O_7^{2-}$ to Cr^{3+}*

An overall equation for the reaction. (The potassium ions are spectators and do not appear in the ionic equation.)

PRACTICE PROBLEM 3

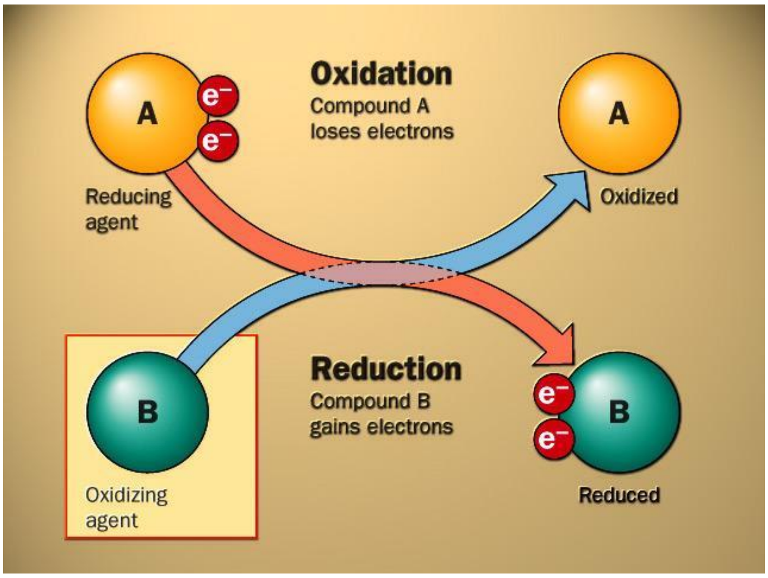
Write the half-equation for the oxidation of sulfur dioxide gas, SO_2, to sulfate ions, SO_4^{2-}, in solution.

Complete the questions Ex 12.2 Q 1-10 and 12.2 Quick quiz, pages 473 - 474

Oxidants and Reductants

An oxidant causes another substance to be oxidised. It itself is simultaneously being reduced, hence undergoing reduction.

A reductant causes another substance to be reduced. It itself is simultaneously being oxidised, hence undergoing oxidation.



Exercises:

Label the oxidant, reductant, what is oxidised, reduced, undergoing oxidation & reduction in the following equation:

$$Cu^{+}_{(aq)} + Br_{2\,(g)} \rightarrow Cu^{2+}_{(aq)} + 2Br^{-}_{(aq)}$$

Finish the half equation for: $Zn(s) \rightarrow Zn^{2+}(aq)$

$2H^{+}(aq) \rightarrow H_2(g)$

Which is the oxidation reaction, reduction reaction?

What is being oxidised, reduced?

What is the oxidant, reductant?

What is oxidising agent, reducing agent?

Conjugate redox pairs

When a substance is oxidised or reduced, the reactant and the product it forms are referred to the conjugate redox pair.

e.g. $Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2e^{-}$

The conjugate redox pair is $Zn^{2+}(aq)/Zn(s)$. The pairs are usually written as oxidant/reductant.

TABLE 16.1.1 Identifying conjugate redox pairs in a redox reaction

	Example 1	Example 2
Overall equation	$Fe(s) + Sn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Sn(s)$	$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$
Oxidation half-equation	$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$
Reduction half-equation	$Sn^{2+}(aq) + 2e^{-} \rightarrow Sn(s)$	$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$
Conjugate redox pairs	$Fe^{2+}(aq)/Fe(s)$ $Sn^{2+}(aq)/Sn(s)$	$Cu^{2+}(aq)/Cu(s)$ $Ag^{+}(aq)/Ag(s)$

Oxidation Numbers

When atoms form new compounds such as: $SO_4^{2-} \rightarrow SO_2$ it is often difficult to tell if sulfur has lost or gained electrons.

The assigning of <u>oxidation numbers</u> to elements helps identify whether it has been involved in a redox reaction. An oxidation number is the imaginary charge an atom would have if it was an ion. They have no physical meaning.

Note: O^{2-} ion has a charge of '2– ' and an oxidation number of '–2'

Rules for Oxidation Numbers

1. The oxidation number of an element or compound is 0
   e.g. for Cu or O_2: ON = 0
2. For simple ions: ON = charge on ion
   e.g. Cl^- = -1, S^{2-} = -2
3. In compounds, elements have 'fixed' ON, except for a few cases:
   a. For hydrogen = +1 (except in metal hydrides = -1)
      e.g. H in NaH has an ON of -1
   b. For oxygen = -2 (except in peroxides = -1)
      e.g. O in H_2O_2 or BaO_2
   c. The sum of the oxidation numbers in a neutral compound is 0
   d. In a polyatomic ion the sum of ON is the charge on the ion

Some more rules…

- The most electronegative element in a compound has the negative oxidation number
  - **Electronegativity F >O > Cl >N > other elements
- The oxidation number of F and Cl are -1
- Group 1 metals have an oxidation number of + 1 , and Group 2 metals + 2
- Oxidation numbers of transition elements and non-metallic elements may vary.

(e.g. N in NH_3 is -3, N in N_2O_5 is +5)

Exercise - Assign Oxidation Numbers for the underlined element below:

H<u>N</u>O₃

<u>C</u>O₃²⁻

<u>F</u>₂O

<u>Mg</u>

Using Oxidation Numbers

- Oxidation involves an INCREASE in oxidation number
- Reduction involves an DECREASE in oxidation number

e.g. $2Cu^{+}_{(aq)} + Br_{2\,(g)} \rightarrow 2Cu^{2+}_{(aq)} + 2Br^{-}_{(aq)}$

Oxidation numbers are used in naming of compounds:

- Fe(III)Chloride , ie Fe^{3+} = +3
- Permanganate (VII) MnO_4^-, ie Mn = +7

Identifying Redox Reactions

If the oxidation numbers of substances have changed then the reaction is a redox reaction. HINT: first look for elements, their oxidation numbers are 0 (easiest)

Exercise - Which reactions are redox? Identify if the following are redox reactions:

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$

$2Ag + Cl_2 \rightarrow 2AgCl$

$FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$

Complete the questions Ex 12.3 Q 1-5 and 12.3 Quick quiz, pages 479 - 480

THE REACTIVITY SERIES OF METALS

Reactivity of metals

Sodium, magnesium and iron are metals that can be easily oxidised. Other metals do not oxidise (corrode) as easily.

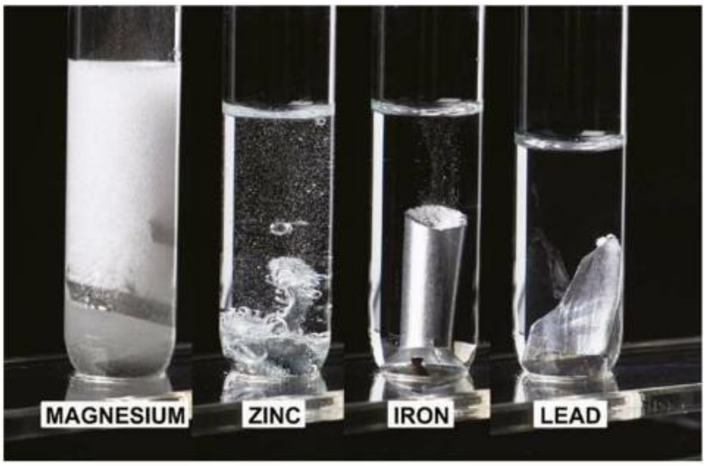


FIGURE 16.2.1 Some metals react with dilute acid to form a salt and hydrogen gas. The reaction between magnesium and dilute acid is extremely vigorous. The reaction between zinc and dilute acid is less vigorous. The reaction between iron and dilute acid is very slow. There is no reaction between lead and dilute acid. Based on this information, the order of metal reactivity from most reactive to least reactive is magnesium, zinc, iron and lead.

Reactivity series

The reactivity series or 'electrochemical series' lists the metals in order of their reactivity. The series lists the reduction half equations for metal cations. As you go down the reactivity series:

- Metal cations (on the left side) become harder to reduce and therefore less likely to react.
- Metals (right side) become more reactive.

Strongest oxidising agent | Weakest reducing agent

increasing oxidising agent strength ↑ | increasing reducing agent strength ↓

$$Au^{+}(aq) + e^{-} \rightarrow Au(s)$$
$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$
$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$
$$Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$$
$$Sn^{2+}(aq) + 2e^{-} \rightarrow Sn(s)$$
$$Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$$
$$Co^{2+}(aq) + 2e^{-} \rightarrow Co(s)$$
$$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$$
$$Cr^{3+}(aq) + 3e^{-} \rightarrow Cr(s)$$
$$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$$
$$Mn^{2+}(aq) + 2e^{-} \rightarrow Mn(s)$$
$$Al^{3+}(aq) + 3e^{-} \rightarrow Al(s)$$
$$Mg^{2+}(aq) + 2e^{-} \rightarrow Mg(s)$$
$$Na^{+}(aq) + e^{-} \rightarrow Na(s)$$
$$Ca^{2+}(aq) + 2e^{-} \rightarrow Ca(s)$$
$$K^{+}(aq) + e^{-} \rightarrow K(s)$$
$$Li^{+}(aq) + e^{-} \rightarrow Li(s)$$

Weakest oxidising agent | Strongest reducing agent

FIGURE 16.2.2 Reactivity series of metals.

Predicting redox reactions

A more reactive metal (lower right of electrochemical series) tends to oxidised and donate electrons to <u>cation of less reactive metal</u> (top left of the electrochemical series).

This is called a metal displacement reaction as metals will <u>displace</u> other metals from solutions of their ions.

It is a spontaneous reaction

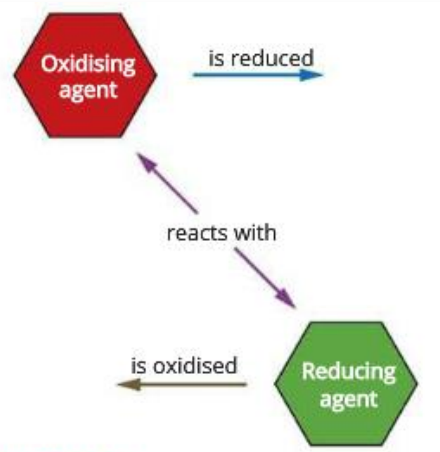


FIGURE 16.2.4 Predicting the reaction between an oxidising agent and a reducing agent.

Example: Predict if zinc will displace copper from a solution containing copper (II) ions and, if appropriate, write the half equations and overall redox equation for the reaction.

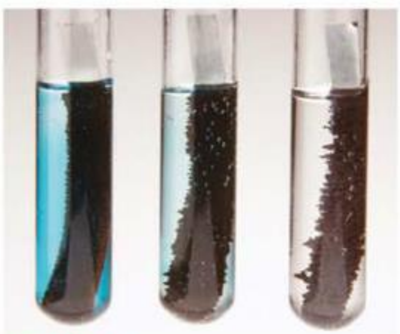


FIGURE 16.2.7 A brown deposit of copper metal is observed forming on the zinc and the blue copper(II) sulfate solution gradually becomes colourless as the concentration of Cu^{2+} ions decreases.

Example: Write the reduction and oxidation half equation and the overall redox equation between Zinc and Copper.

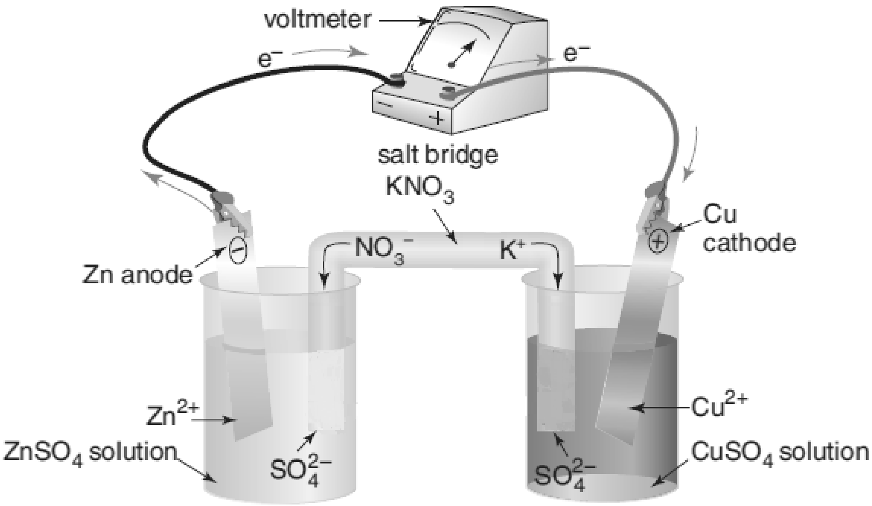
Predicting redox reactions

When a piece of nickel (Ni) is placed in a solution of silver nitrate (Ag^{+}), will there be a reaction?

Complete 12.4 Quick Quiz and Exercise 12.4 Q 1 - 10, pages 484 - 485

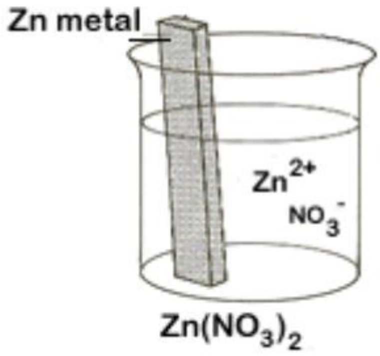
GALVANIC CELLS

Galvanic cells can be used to convert chemical energy into electrical energy. The electric current is formed from a **spontaneous redox reaction** between two half cells.



GLB

Half cells



Each half cell contains an electrode and an electrolyte. The electrolyte is a solution that contains free moving ions. The electrode is an electronic conductor that has delocalised electrons that can move through the circuit. The species present in each half cell form a **conjugate redox pair**.

The electrode at which oxidation takes place is called the **anode.**

The electrode at which reduction takes place is called the **cathode.**

AN OIL RIG CAT

In galvanic cells:

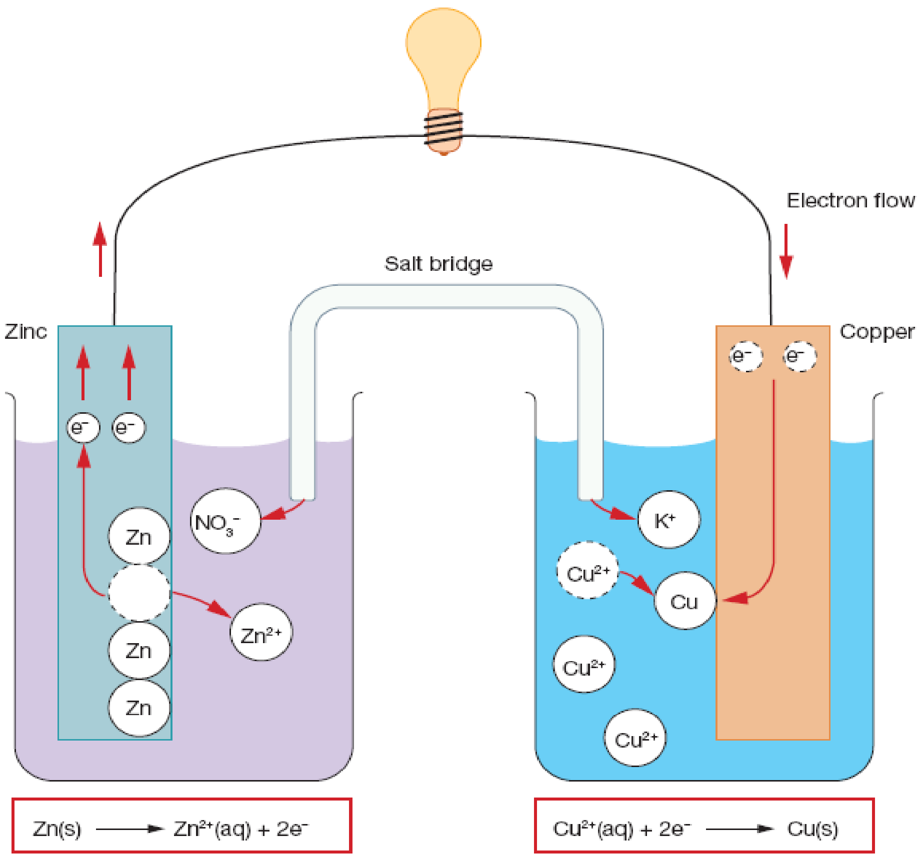
- Ca**+**hode is always POSITIVE
- A**N**ode is always NEGATIVE

The Salt Bridge

The purpose of the salt bridge is to provide ions to balance the charges that form in the half cells. If there is no salt bridge is present, half cells would accumulate charge as the reaction proceeds, restricting the extent of the reaction and production of electricity. Salt bridges are usually made of filter paper or paper towel soaked in an ionic compound such as KNO_3. The flow of ions in the salt bridge enables the circuit to be complete and the movement of ions compensates for those lost or gained during the redox reactions in the half cell.

In general:

- Anions migrate towards the anode
- Cations migrate towards the cathode



Example: Draw a labelled Zn^{2+}/Zn and H^+/H_2 galvanic cell. You must label:

- *The solution and electrodes*
- *The half equations*
- *The overall redox equation*
- *The anode and the cathode and hence which undergoes oxidation and reduction*
- *The direction of electron flow*
- *The ions of the salt bridge and direction of movement*

CORROSION

Dry Corrosion

Dry corrosion occurs as a consequence of a metal reacting with oxygen in the air to form a metal oxide. Sometimes referred to as direct corrosion

e.g. $4Na\ (s) + O_2\ (g) \rightarrow 2Na_2O\ (s)$

Dry corrosion of aluminium can be useful to protect the metal in situations where maintenance is difficult

e.g. Aluminium oxide coating on an aluminium window.

Dry corrosion in iron, however, forms a coating of iron oxide that flakes off easily, leaving the metal exposed.

Wet Corrosion

Wet corrosion can occur in moist air or through direct immersion in water. Water can accelerate the corrosion of iron. In general, corrosion is accelerated by:

- The presence of water
- Impurities such as salt and acidic pollutants that dissolve in water.

Corrosion can be reduced when the metal is alloyed with other materials that have a protective coating.

The wet corrosion process

Step 1: Iron is oxidised to form Fe^{2+} ions at one region on the iron surface:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

At the same time at another region on the surface, using the electrons produced by the oxidation process, oxygen is reduced in the presence of water to hydroxide ions:

$$O_2(aq) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

The overall equation for step 1 is:

$$2Fe(s) + O_2(aq) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq)$$

Step 2: The formation of a precipitate of iron(II) hydroxide:

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$$

Step 3: Further oxidation of iron(II) hydroxide occurs in the presence of oxygen and water to produce iron(III) hydroxide, a red-brown precipitate:

$$4Fe(OH)_2(s) + O_2(aq) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$$

Step 4: In air, the iron(III) hydroxide loses water to form hydrated iron(III) oxide ($Fe_2O_3.xH_2O$), which is known as rust.

Prevention of corrosion

There are several ways to prevent corrosion:

- Surface protection - covering the surface of the iron to prevent contact with oxygen and moisture.
  - Alloying – oxidation still occurs but will form a protective layer
  - Electroplating – Iron is coated with a thin layer of a less reactive metal
- Electrochemical protection
  - Cathodic protection – uses low voltage DC to give the ion a negative charge. Iron will be gaining electrons, therefore oxidate is inhibited.
  - Sacrificial protection – galvanised iron (iron coated in zinc). Zinc is more readily oxidised than iron so will undergo oxidation first (it is sacrificed).

Chapter 12.5 Quick quiz

Chapter 12.5 Exercise questions 1 - 10, pages 496 - 497

Review Q 12.6 Q 1 - 10 Page 499 - 500