CHEMISTRY NOTES

SUBJECT: Chemistry
LEVEL: Higher
TEACHER: Tara Hogan

Topics Covered:

- Organic Chemistry (Fuels) - Oil refining, natural gas, petrol, preparation of ethene and ethyne.
- Oxidation & Reduction – oxidation and reduction, oxidation numbers, rules for oxidation numbers, balancing redox equations

About Tara:
Tara has been teaching Higher Level Chemistry at The Institute of Education since 2001. During this time many of her students have achieved excellent results with one of her students receiving the highest grade in Chemistry in Ireland. Her aim is to make her subject clear, accessible and interesting so that students will want to continue studying Chemistry.

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OIL REFINING AND ITS PRODUCTS

CRUDE OIL (PETROLEUM)

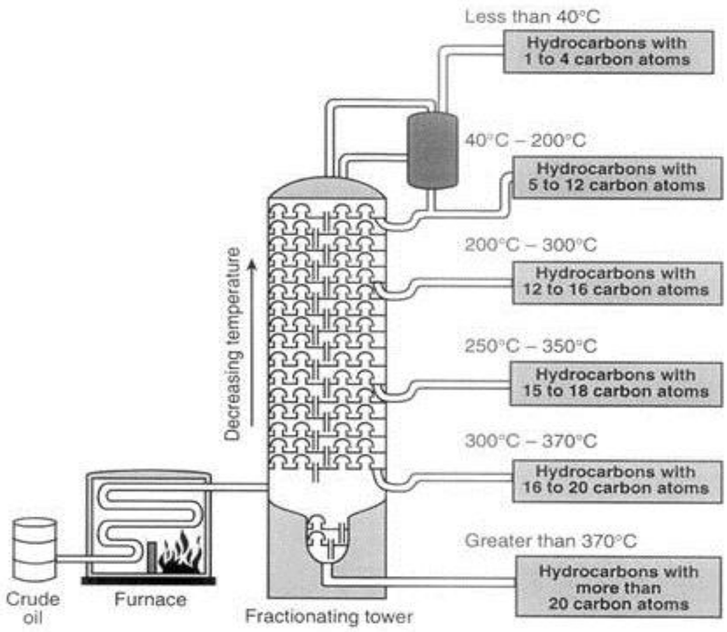
1. Crude oil is a fossil fuel. It is formed by the decomposition of dead bodies of creatures that died millions of years ago.
2. It is pumped from under the ground or sea
3. It is a thick, black, viscous, pungent liquid and is of little or no use in this form.
4. It is found in large quantities in countries like Iran, the North Sea, the USA, Russia etc.

COMPOSITION OF CRUDE OIL

It consists of a **mixture of hydrocarbons**. Mixture means not chemically combined.
The types of hydrocarbons present in oil depends on where it is found in the world. The hydrocarbons may be small chained molecules e.g. ethane, or may consist of many carbon atoms. The smaller hydrocarbons are volatile (low b.p.) and are used as fuels or chemical feedstocks while the larger ones are heavy and may be used in heavy industry or may be broken down into smaller molecules we will see later (thermal or catalytic cracking).

FRACTIONATION OF CRUDE OIL

Fractional distillation is a process that is used to separate the crude oil into its components. This method can be used as the oil is a mixture of molecules. The principle involved is that the oil is **separated into 'fractions' on the basis of the different boiling points** of the compounds. These 'fractions' are now more useful and can be used for various purposes.



STAGES

1. The crude oil is heated to high temperatures and is fed into large fractionating towers. These towers may be 80 m high.
2. The tower is kept at a high temperature at the bottom.
3. As you go up the tower there are trays present to collect the 'fractions'.
4. The temperature **decreases** as you ascend the tower.
5. As the crude oil rises up the tower the fractions will reach a temperature that is **just below their boiling point** and turn into liquids which collect on the tray.
6. The heavier hydrocarbons will condense first, while the lighter hydrocarbons will rise higher and condense higher up the tower.

THE FRACTIONS AND THEIR USES

NAME OF FRACTION	CARBONS	USES
Gas B.P – 25 ° C to 40 ° C	$C_1 - C_4$	Refinery fuel Liquefied to form propane or butane gas (LPG).
Light gasoline B.P. – 40 ° C to 75 ° C	$C_5 - C_{10}$	Motor fuel
Naptha (v. important) B.P. – 75 ° C to 150 ° C	$C_7 - C_{10}$	**Petrol** Feedstock for petrochemical industry
Kerosene B.P. – 150 ° C to 240 ° C	$C_{10} - C_{14}$	Fuel for planes Paraffin lamps/stoves
Gas oil and heavy gas oil B.P. – 240 ° C to 500 ° C	$C_{14} - C_{40}$	Diesel oil Lubricating oil for engines
Residue B.P. - > 500 ° C	C_{35} and upwards	Heavy industrial fuel Used in catalytic cracking Bitumen for road surfaces

NATURAL GAS

1. Natural gas is a mixture of hydrocarbons.
2. Usually made up of methane, ethane, propane and butane.
3. The North Sea and Kinsale gas fields are made mainly of methane (95%).
4. In the USA natural gas mainly consists of propane and butane.
5. Propane and butane are sold as **liquefied petroleum gas (LPG**) in Europe.
6. As natural gas is odourless for safety reasons compounds called **MERCAPTANS** (usually sulfur containing compounds) are added to the natural gas before distribution. Mercaptans have a strong smell so this alerts to a leakage.

PETROL

In order for the engines in cars to run smoothly petrol and oxygen react and this produces the power to turn the wheels of the car.
The petrol and oxygen must ignite and explode evenly at the correct time to ensure the engine runs smoothly.

- **Auto – ignition ('knocking')** - Sometimes this reaction between the petrol and air can happen too soon due to increased pressure in the engine and auto-ignition occurs – this is also called 'knocking'. 'Knocking' happens if the petrol and oxygen explode due to an increase in pressure in the engine instead of the explosion being caused by a spark (from the spark plugs!). This can damage the engine and lead to loss of power.
- If the petrol is rich in straight chained hydrocarbons i.e. hexane or octane, auto-ignition occurs. So straight chained hydrocarbons are the problem.
- **Petrol rich in branched chained hydrocarbons burns more smoothly and efficiently. An example of a branched-chained hydrocarbon is 2,2,4-trimethylpentane (iso-octane). Draw the structural formula of this compound.**

OCTANE NUMBER

Defn- the measure of the tendency of a fuel to resist auto-ignition

- **2,2,4-trimethylpentane (iso-octane)** is one of the most efficient so it is given an octane number of 100. This type of petrol does not auto-ignite or 'knock'. (Note - Heptane is given an octane value of 0!)
- In straight chained hydrocarbons, the **shorter the alkane** the higher the octane number.
- In branched-chained hydrocarbons, the **greater the number of branches** the higher the octane number.
- **Cyclic and aromatic hydrocarbons** also have a high octane number.
- A 'good' quality petrol can have an octane number of 97.

Structural features of alkanes that prevent autoignition -

1. Short chained
2. Highly branched
3. Cyclic.

SOLUTIONS TO AUTO-IGNITION (KNOCKING)

1. **Add lead to the petrol (additive)**. Lead was added in the form of **tetraethyl lead**. This allowed the petrol to burn smoothly. However, leaded petrol is toxic, therefore harmful to the environment and people's health. Leaded petrol is being phased out due to these reasons.
2. **Isomerisation (reforming)** – this involves changing straight-chained hydrocarbons into branched-chained isomers. The branched-chained isomers burn more smoothly and therefore have a higher octane number.
3. **Dehydrocyclisation (reforming)** – this process involves the conversion of straight-chained hydrocarbons to form ring compounds. The ring compounds are then converted into aromatic compounds. This is done in the presence of a catalyst. As hydrogen is a by-product of this reaction it is called 'dehydro'. Aromatic compounds have a high octane number but are also carcinogenic.
4. **Catalytic cracking (reforming)** – this process involves breaking down long chained hydrocarbons for which there is low demand into short chained molecules for which there is high demand. These short-chained hydrocarbons have a higher octane number and also tend to be highly branched.
5. **Addition of oxygenates (additive)** - this is the addition of oxygen compounds to the petrol. These tend to be of two types (a) **addition of alcohols** i.e. methanol (octane no. of 114) and (b) **addition of ethers** i.e. methyl tert-butyl ether (MTBE) (octane no. of 118). These compounds (a) increase the octane number of the petrol and (b) **they also cause less pollution as they reduce the level of carbon monoxide in the exhaust fumes.**

Whichever process or combination of processes are used to improve the octane number is dependant on the cost!! Unleaded petrol is more expensive to produce than leaded petrol but the latter is being phased out due to public pressure.

REFORMING
Defn – reforming involves changing straight chained hydrocarbons into branched chained hydrocarbons or cyclic hydrocarbons.

CRACKING
Defn – cracking involves changing long chained hydrocarbons for which there is low demand, into short chained hydrocarbons for which there is high demand.

AUTO-IGNITION
Defn – the early explosion of a petrol-air mixture caused by increasing pressure in the engine.

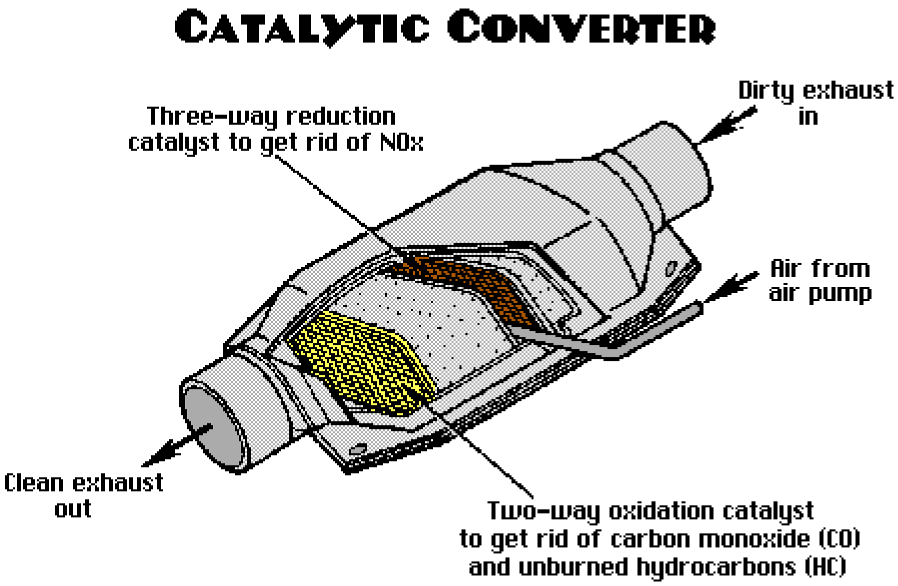
OCTANE NUMBER
Defn – the octane number of a fuel is the measure of its tendency to resist 'knocking'.

CATALYTIC CONVERTERS IN CARS

- A catalytic converter is fitted to car exhausts to reduce pollution from the exhaust fumes.
- Exhaust fumes contain **carbon monoxide, nitrogen monoxide, nitrogen dioxide** and **lead compounds** if leaded petrol is used. It also contains **unburned hydrocarbons.**
- The catalytic converter changes these harmful gases into harmless gases.

$$CO + NO \rightarrow CO_2 + \frac{1}{2}N_2$$

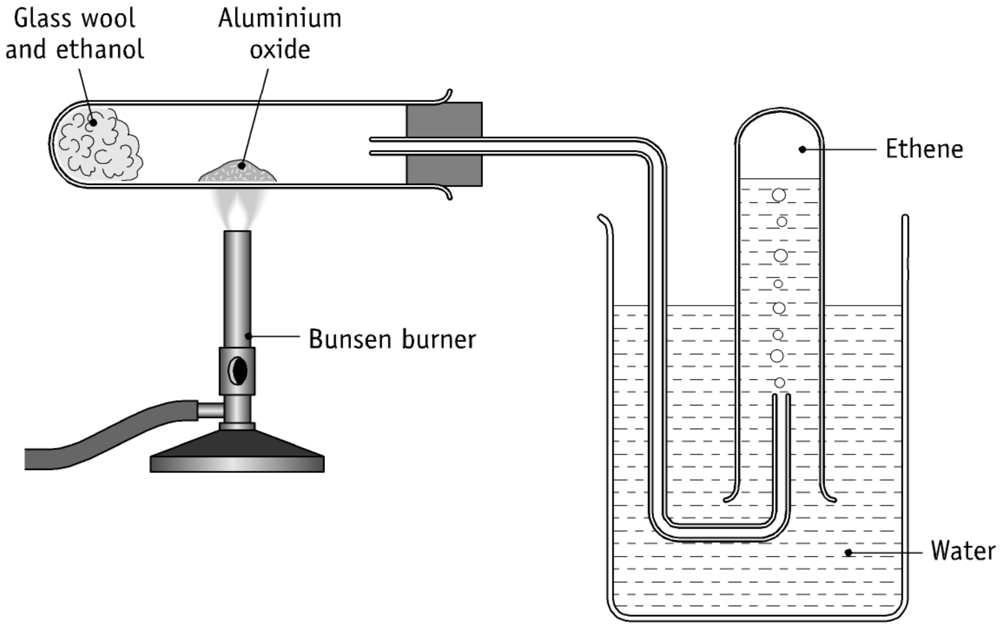
- The catalytic converter contains catalysts such as **platinum, palladium and rhodium** inside a stainless steel case. The inside of the converter looks like a honeycomb. This honeycomb arrangement allows for a **large surface area** so increased removal of harmful gases into harmless gases such as carbon dioxide and nitrogen..
- The lifetime of a converter is dependent on the type of petrol used. If leaded petrol is used then the lifetime of the converter is shorter than if unleaded petrol is used. The lead poisons the catalysts.
- It is policy in the EU since 1993 that all new cars are fitted with catalytic converters.



ETHENE

Ethene is a very important organic compound as it is the 'building block' from which many plastics are made.
In the laboratory, ethene is prepared by a **dehydration reaction** of **ethanol.** Dehydration means removing water.
This is an example of an **elimination reaction**.

EXPERIMENT – THE PREPARATION OF ETHENE



Equation - $C_2H_5OH \xrightarrow[-H_2O]{Al_2O_3} C_2H_4 + H_2O$

Apparatus – boiling tube, retort stand, glass tubing, water bath, test tubes, Bunsen burner, rubber bung.

Materials – ethanol, aluminium oxide, water.

Method –

1. Some ethanol is poured into a boiling tube.
2. **Glass wool** is pushed down into the tube to (a) **soak up the ethanol** and (b) to **hold the ethanol in place** at the end of the tube during the experiment as it is a liquid.
3. The boiling tube was clamped in a horizontal position using the retort stand.
4. Some **aluminium oxide** (white powder) is placed half way along the tube. Aluminium oxide is the dehydrating agent/catalyst for the reaction.
5. The tube is stoppered with a rubber bung and glass tubing is attached through the rubber bung into the water bath.

6. A test tube is filled with water and placed in the water bath as shown in the diagram.
7. A Bunsen burner is placed under the aluminium oxide and is lit to give a blue flame.
8. The heat from the Bunsen burner vaporises the ethanol and as it passes over the aluminium oxide the ethanol is dehydrated to produce ethene.
9. The first test tube collected will have a low yield of ethene, as it will mainly consist of displaced air from the boiling tube.
10. Collect 5 more test tubes of ethene and stopper them.
11. **N.B. - Before turning off the Bunsen burner it is very important to remove the glass tubing from the water bath to prevent 'suck back'**. If the tubing was left in the water bath, once the heat is removed the gases in the boiling tube would contract and this would cause water to be drawn back into the boiling tube to balance the drop in pressure which would cause the boiling tube to shatter.
12. **Other precautions include** – keep gas away from flames as gas is flammable and there is a risk of explosion, wear safety glasses, use of tongs when handling glass wool.

PROPERTIES OF ETHENE GAS

1. **Physical appearance** – colourless gas with a sweetish smell.
2. **Solubility in water** – the gas is insoluble in water as water is a polar solvent and ethene is non-polar therefore ethene does not form hydrogen bonds with water. This is why ethene can be collected by the displacement of water.
3. **Combustion** – when a lighted taper is placed in a test tube of ethene, **a luminous flame** is observed. A small amount of smoke may also be produced. If limewater is added after burning, the limewater goes 'milky'. What does this prove? Write a balanced equation for the combustion of ethene gas -

4. Tests for unsaturation:

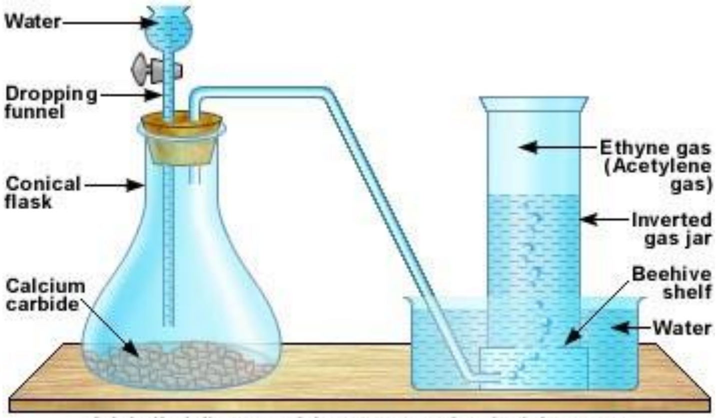
(a) **Addition of bromine water** – bromine water is a red/brown colour. When bromine water is added to ethene an *addition reaction* occurs. The bromine adds across the double bond to form 1,2-dibromo ethane. This colour change from **red-brown to colourless** proves that ethene is unsaturated.
Equation - $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$

(b) **Addition of dilute potassium manganate (VII)** – a dilute solution of potassium manganate (VII) is **light purple** in colour. When this solution is added to ethene gas and shaken the purple colour of the solution goes **colourless**. This test also proves the presence of the carbon – carbon double bond, thus proving that ethene is unsaturated.

ETHYNE

Ethyne is used for cutting and welding metals as when burned in oxygen it can reach temperatures over 3000 ° C.

EXPERIMENT – PREPARATION OF ETHYNE



A labelled diagram of the apparatus for the laboratory preparation of ethyne or acetylene.

Equation - $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$

Calcium dicarbide reacts with water to produce ethyne and calcium hydroxide.

Apparatus – dropping funnel, Buchner flask, glass tubing, conical flask, two holed rubber bung, test tubes, water bath.

Materials – calcium dicarbide, water, [acidified copper (II) sulfate solution.]

Method –

1. Set up the apparatus as shown in the diagram.
2. Do not touch the calcium dicarbide as sweat from hands may start the reaction.
3. Note that the **calcium dicarbide** is a **greyish solid.**
4. Slowly add the water from the dropping funnel.
5. Note **effervescence** (fizzing) as the water reacts with the calcium dicarbide.
6. Also note the production of calcium hydroxide in the Buchner flask. This appears as a white suspension (foamy).
7. The first gas jar collected will have a low yield of ethyne, as it will contain mainly displaced air from the Buchner flask. Discard this carefully.
8. Collect 4 test tubes of ethyne gas.

Important notes –

(a) Impurities are present in the calcium dicarbide. These solid impurities are calcium phosphide, Ca_3P_2 and calcium sulfide, CaS .

(b) These solid impurities give rise to gaseous impurities in the ethyne gas collected. The gaseous impurities are phosphine, PH_3 and hydrogen sulfide, H_2S .

(c) The gaseous impurities are removed by bubbling the impure ethyne gas through acidified copper (II) sulfate solution.

PROPERTIES OF ETHYNE GAS

1. **Physical properties** – ethyne is a colourless gas with a sweetish smell if pure.
2. **Solubility in water** – ethyne is insoluble in water, as water is a polar solvent and ethyne being non-polar does not form hydrogen bonds with water. This is why ethyne can be collected by the displacement of water.
3. **Combustion** – N.B. very dangerous and must be done in a fume cupboard!! Ethyne burns with a **smoky luminous flame**. The smoke is due to unburned carbon (very sooty). To ensure no soot use an excess of oxygen when burning. Write a balanced equation for the combustion of ethyne:____
4. **Tests for unsaturation** –

(a) **Addition of bromine water** – when bromine is added across the carbon-carbon triple bond the red-brown colour of the bromine goes colourless thus proving that the ethyne is unsaturated. An equation showing this reaction was asked in 2003.

(b) **Addition of dilute potassium manganate (VII)** – the purple colour of the manganate (VII) solution goes colourless also proving the presence of a multiple bond (carbon-carbon triple bond) hence ethyne is unsaturated.

WORK SHEET

1.

(a) Draw a labelled diagram of the apparatus you would use to produce and collect ethyne in the laboratory.
(b) Phosphine gas often occurs as an impurity in ethyne. How would you remove the phosphine from the ethyne?
(c) Ethyne is often described as an *unsaturated hydrocarbon*. Explain the two words in italics.
(d) Name the reagent you would use to show that ethyne is unsaturated and describe what you would observe when this reagent is applied to a sample of ethyne gas and shaken.
(e) Describe what you would see if ethyne is burned in air? Write a balanced equation for this reaction.
(f) Give a wide scale use of ethyne. (Folens sample papers)

2.

(a) Petrol is obtained from crude oil in an oil refinery. Name the process used to obtain the petrol from the crude oil.
(b) Give the name and structural formula of the substance found in petrol that is given an octane number of 100.
(c) What is meant by octane number?
(d) What lead compound used to be added to petrol? Explain why it was added to the petrol and give a reason why it is no longer added to petrol.
(e) Name two features of the structure of alkanes that would make them less prone to knocking.
(f) Oxygenates are often added to petrol. Give an example of an oxygenate and explain why it is added to petrol.
(g) Explain the term catalytic cracking and briefly say why it is used. (Folens sample papers)

3.

(a) Draw diagrams to represent the structure of (i) benzene and (ii) methylbenzene.
(b) Methylbenzene is often used in the laboratory in preference to benzene. Give a reason for this.
(c) Benzene and methylbenzene are described as aromatic compounds. What does aromatic mean?
(d) $CH_3CHBrCH_3$ (A) $CH_3CH_2CH_2OH$ (B)

Name the above compounds A and B.

(e) Compound B can undergo an elimination reaction. Write an equation for this reaction. Name the reagents involved and give another name for this type of reaction.
(f) Outline the mechanism for the reaction between bromine and ethene.
(g) Is benzene soluble in water? Give a reason for your answer.

Note – part (f) of this question is to be covered in a later hand out.

4.

(a) Describe what you would expect to see if a test tube of ethyne is burned in air.
(b) Ethyne is an unsaturated compound. Describe how you could demonstrate this in the laboratory.
(c) Write an equation for the combustion of methane in excess air. Where are you most likely to encounter methane in your everyday life?
(d) What are mercaptans used for?

5.

(a) Oil refining separated crude oil into a number of different fractions. Discuss the industrial process (included in your answer should be some named fractions and their use).
(b) Outline a use for mercaptans.
(c) Define octane number.
(d) Discuss methods of improving the efficiency in the internal combustion engine when a mixture of petrol and air is drawn into the cylinder and ignited by a spark.
(e) By using alternatives to lead, how can we say that the combustion of petrol becomes more environmentally friendly?
(f) Name two elements used as catalysts in the catalytic converters in cars.

6.

(a) The compounds octane and 2,2,4-trimethylpentane (iso-octane) are <u>structural isomers.</u> Explain what is meant by the underlined term.
(b) Why is it possible to separate these isomers by fractional distillation?
(c) Draw the structural formula of 2,2,4-trimethylpentane.
(d) Suggest two structural features of hydrocarbons that contribute to them having a relatively high octane number.
(e) Name one additive or type of additive other than lead that can be added to petrol to increase its octane number.

7.
(a) Write a balanced equation for the production of ethyne in the laboratory.
(b) Give the name or formula of an impurity present in the ethyne gas produced.
(c) Give the name or formula of a compound present that would have given rise to this impurity.
(d) Suggest a way of removing the gaseous impurity from the ethyne gas produced.
(e) Give an everyday use of ethyne.

LEAVING CERT 2002

Classify C_3H_6 as having one, two or three tetrahedrally bonded carbon atoms. (3)

LEAVING CERT 2002

The following hydrocarbons can all be used as fuels.

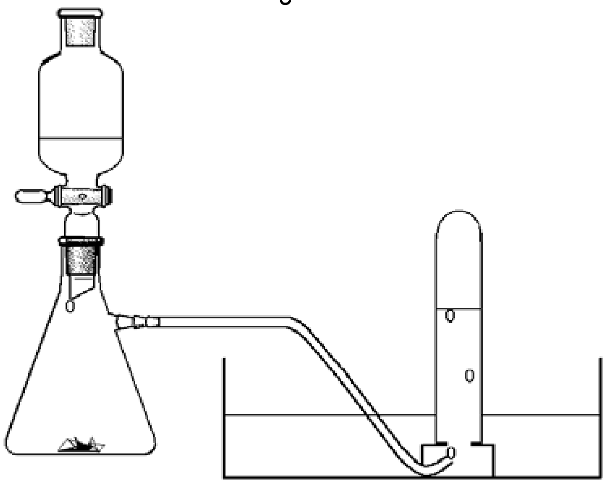
Methane (CH_4) butane (C_4H_{10}) 2,2,4-trimethylpentane (C_8H_{18})

(a) Butane is a major component of LPG. What do the letters LPG stand for?(5)
Draw two structural isomers of butane.(6)

(b) Methane is a major component of natural gas. Why are mercaptans added to natural gas? What environmental change or effect is associated with the release of methane to the atmosphere? Apart from leaking pipes, name a major source from which methane is released to the atmosphere.(9)
(c) What structural feature of 2,2,4-trimethylpentane results in it having a high octane rating? Give one other structural feature which increases the octane number of a hydrocarbon. (6)

LEAVING CERT 2003

The diagram shows an apparatus that can be used for the preparation of ethyne gas, C_2H_2.
A liquid X is dropped onto the solid Y and the gas collected in test tubes as shown



(a) Identify the liquid X and the solid Y. (8)
(b) Describe the appearance of solid Y.(3)
(c) Write a balanced equation for the reaction between X and Y producing ethyne. (6)

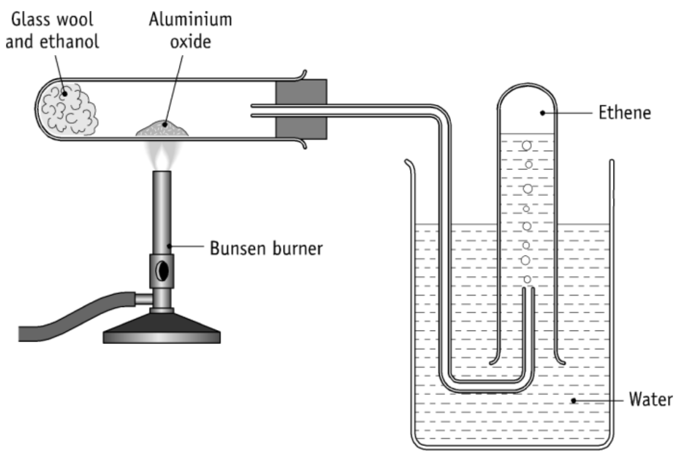
(d) What is observed when a sample of ethyne gas is burned in air? Write a balanced equation for the combustion of ethyne in oxygen.(9)

(e) Ethyne, C_2H_2, is described as an unsaturated hydrocarbon.
Describe a test you could carry out to show that ethyne is unsaturated.
Write an equation for the reaction taking place. Name the organic product (18)

(f) The common name for ethyne gas, C_2H_2, is acetylene. Give one major use of the gas. (6)

LEAVING CERT 2004

The diagram shows the experimental set up used by a group of students to prepare a sample of ethene from ethanol and to collect the ethene produced.



(a) What is the function of the glass wool?(5)

Identify the solid X and describe its appearance. (6)

(b) State and explain two safety precautions which should be observed when carrying out the student experiment. (12)

(c) Write a balanced equation for the reaction involved in this preparation. (6)

(d) If the ethene produced is bubbled through an acidified solution of potassium manganate (VII), the solution is decolourised showing that ethene is *unsaturated.* What is meant by the term *unsaturated*? Describe how you would carry out another test to confirm that ethene is unsaturated. (12)

(e) Describe the flame that would be observed when a combustion test is carried out on a sample of ethene gas. Write a balanced equation for the combustion of ethene in excess oxygen. (9)

LEAVING CERT 2005 Q7

Describe with the aid of a labelled diagram how the conversion of W (ethanol to ethene) may be carried out in a school laboratory and how a sample of the product may be collected. How would you test this product to show that it is unsaturated. (18)

LEAVING CERT 2006 Q9

Ethene may be made in a school laboratory using the arrangement of apparatus drawn.

(i) Give the name and formula of the solid A which is heated using the Bunsen burner. (6)

(ii) Identify the solid B which is used to keep the ethanol at the end of the test tube. (3)

(iii) What precaution should be observed when heating is stopped? Why is this necessary? (6)

(iv) Give one major use of ethene gas. (3)

LEAVING CERT 2007

Useful hydrocarbons are obtained by the fractional distillation of crude oil, which itself has little or no direct use. Hydrocarbons are excellent fuels.

(a) In which fraction of crude oil do pentane and its isomers occur? (5)

Give the systematic (IUPAC) name of each of the structural isomers of pentane shown below. (9)

Which of these isomers would you predict to have the lowest octane number? Justify your choice in terms of the structural features of the molecules. (9)

Write a balanced equation for the combustion of pentane (C_5H_{12}) in excess oxygen. (6)

(b) Naphtha and gas oil are two of the hydrocarbon fractions obtained from the fractional distillation of crude oil. How do the molecules of the naphtha fraction differ from the molecules of the gas oil fraction? (3)

Explain with the aid of a labelled diagram how naphtha (b.p. approximately 100 $^\circ$ C) is separated from gas oil (b.p. approximately 300 $^\circ$ C) in the fractional distillation of crude oil. (9)

Bitumen is a residue fraction obtained from crude oil. Give one use for bitumen. (3)

(c) What is catalytic cracking? What is its economic importance in oil refining? (6)

LEAVING CERT 2008

(a) The hydrocarbon molecules in petrol typically contain carbon chains with between five and ten carbon atoms. The most widely used petrol in Ireland has an octane number of 95.

(i) What is meant by the octane number of a fuel? (5)

(ii) The two hydrocarbons used as references when establishing the octane number of a fuel are heptane and 2,2,4 – trimethylpentane. Draw the structure of each of these molecules. (6)

(iii) Crude oil is separated into a number of fractions in oil refining. Name the two fractions which contain molecules with the carbon chain lengths needed for petrol. (6)

(iv) Dehydrocyclisation is one of the processes used to increase the octane numbers of hydrocarbons. What two changes to the hydrocarbon molecules occur during this process?(6)

(v) Ethanol is an example of an oxygenate. Give another example of an oxygenate. Give two reasons why oxygenates are added to petrol. (9)

LEAVING CERT 2009

2. Ethene can be prepared in the school laboratory using the arrangement of apparatus shown in Diagram 1.
Ethyne can be prepared in the school laboratory using the arrangement of apparatus shown in Diagram 2.

See exam papers for diagrams

(*a*) Give the name or chemical formula of the solid **X** used in the preparation of ethene.
What is the colour of this solid? (5)
(*b*) Write a balanced equation for the reaction involved in the preparation of ethene. What term describes this type of reaction? (6)
(*c*) State **three** precautions that should be observed when carrying out the preparation of ethene by this method. (9)
(*d*) Give the name or formula of the solid **Y** used in the preparation of ethyne in the school laboratory. Describe the appearance of this solid. (6)
(*e*) Both ethene and ethyne are described as *unsaturated*.
What does this mean? Describe a test you could carry out on a sample of either gas to show that it is unsaturated. What would you observe during the test? (9)
(*f*) Both ethene and ethyne can be burned in air.
What is the most noticeable difference seen when these combustions are carried out in a school laboratory? Write a balanced equation for the complete combustion of either gas. (9)
(*g*) Give (*i*) a major use of ethene,
(*ii*) a major use of ethyne. (6)

LEAVING CERT 2014

6. The fuel in camping gas cylinders, like the one pictured on the right, is a liquefied mixture of propane, butane, and another compound which is a structural isomer of butane.

(*a*) Name the homologous series to which propane and butane belong. Draw the structural formula of propane. (8)

(*b*) Propane and butane have boiling points of –42.1 °C and –0.5 °C, respectively. Explain why propane has a lower boiling point than butane. (6)

(*c*) (*i*) What is meant by saying that compounds are *structural isomers*? (*ii*) Draw the structural formula of the isomer of butane. (12)

Before the discovery of electrons, reactions that involved the addition of oxygen to a substance were described as oxidation reactions. For example the burning of coal, which is carbon, to produce carbon dioxide was an oxidation reaction or the rusting of iron to produce iron oxide. Removing oxygen from a substance was described as a reduction reaction as the mass of the substance got smaller due to the oxygen being removed.
However, after the discovery of the electron scientists examined reactions more closely and noticed that many chemical reactions involved the transfer of electrons. One substance lost electrons while another gained electrons.

OXIDATION
Defn - Oxidation of an element occurs when the element loses electrons.

REDUCTION
Defn - Reduction of an element occurs when the element gains electrons.

A useful way of remembering this is **OIL RIG** – oxidation is loss, reduction is gain.

Both oxidation and reduction occur at the same time. If one element loses electrons, another element gains electrons. These types of reactions are called **REDOX** reactions.

Example 1 $Mg + O \rightarrow Mg^{2+} + O^{2-}$

In the above example we can see that the Mg atom looses 2e to become the Mg^{2+} ion.
The O atom gains 2e to become the O^{2-} ion.

Example 2 $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Identify the species being oxidised? ______________
Identify the species being reduced? ______________

In the above examples the element that loses the electrons is called the **REDUCING AGENT** and the element that gains the electrons is called the **OXIDISING AGENT**.

So to summarise,

Oxidising agents are always themselves reduced as they gain electrons and
Reducing agents are always themselves oxidised as they lose electrons.

If we examine example 1 we can see that Mg is the reducing agent (as it is being oxidised) and O is the oxidising agent (as it is being reduced).

Trial question – in the following equation pick out the species being oxidised, the species being reduced, the oxidising agent and the reducing agent.

$$Fe^{2+} + Cl \rightarrow Fe^{3+} + Cl^{-}$$

Answer-
________ is oxidised
________ is reduced
________ is the reducing agent
________ is the oxidising agent

Note – the species being oxidised/reduced and the oxidising agent/reducing agent are always on the left hand side of the equation as they are reactants.

OXIDATION NUMBERS

A more useful way of keeping track of the movement of electrons can be done using oxidation numbers. These are numbers given to elements so that we can see by how much these elements are oxidised or reduced on going from the left side of the equation to the right side of the equation.

OXIDATION NUMBER
Defn – the oxidation number of an element is the charge an element has or appears to have when it is in a compound when certain rules are applied.

In order to do this we must pretend that all compounds are ionic in their bonding (eventhough we know that this is not true!!). This is what we mean by 'appears to have' in the above definition.

- **For this purpose the less electronegative element becomes positive (loses electrons) and**
- **The more electronegative element becomes negative (gains electrons).**
- **It is important to keep electronegativity values in mind so keep your electronegativity table open.**

To make oxidation numbers easier there are rules that we must learn (unfortunately) so as to be able to give each element the correct oxidation number.

RULES FOR OXIDATION NUMBERS

RULE 1 – Simple elements i.e. those that are not with any other element, have an oxidation number of zero.
Examples – Na, Mg, Fe all have a oxidation number of 0, as does H in the molecule H_2, and O in the ozone molecule O_3.

RULE 2 – In the combined state, Group 1 elements always have an oxidation number of +1 and Group 2 elements always have an oxidation number of +2.
Examples – $NaCl$ – Na has an oxidation number of +1
MgF_2 – Mg has an oxidation number of +2
Ca_3P_2 – Ca has an oxidation number of +2

RULE 3 – In simple ions i.e. <u>single element ions</u>, the oxidation number of the ion is equal to the charge on the ion.

Examples – Na^+ - the oxidation number of the ion is +1

Br^- - the oxidation number of the ion is –1

Fe^{3+} - the oxidation number of the ion is +3

RULE 4 – the halogens (Group 7) in compounds where the <u>halogen is</u> <u>bonded to ONE other element</u> , has an oxidation number of –1, unless the halogen is bonded to a more electronegative element, then the oxidation number will be +1.

Examples – KF – F has an oxidation number of –1

$NaCl$ – Cl has an oxidation number of –1

* Cl_2O – Cl has an oxidation number of +1 as O is more electronegative than Cl.

Note – this rule does not work for halogens in complex ions!! The charge in a complex ion represents a missing element.

RULE 5 – Oxygen usually has an oxidation number of –2: except in the compound OF2 it is +2 as F is more electronegative element than O and in the peroxide ion [O_2^{2-}] where O has an oxidation number of –1.

Examples – Na_2O – O has an oxidation number of –2

H_2SO_4 – O has an oxidation number of –2

* OF_2 – O has an oxidation number of +2 as F is more electronegative

* H_2O_2 – O has an oxidation number of –1 as this is a peroxide

Note – peroxide molecules contain just two elements (one being oxygen!). The metal will be written first in the formula and tend to come from group one or two. There are only two oxygen atoms in any peroxide molecule.

RULE 6 – Hydrogen has an oxidation number of +1 in its compounds : except when it is combined to an element less electronegative than it because then it is a hydride and has an oxidation number of –1

Examples – H_2O – H has an oxidation number of +1

HNO_3 – H has an oxidation number of +1

* NaH – H has an oxidation number of –1

Note – in a hydride molecule, there are two elements in the molecule and hydrogen is written last. Also the metal element will have a lower electronegativity value that hydrogen.

RULE 7 – In <u>complex ions</u> i.e. where more than one element is in the ion, the oxidation numbers must <u>add up to the charge on the ion</u>.

Examples –

Question - What is the oxidation number of N in the ion NO_3^- ?

Solution –

- The oxidation numbers must add up to –1 as this is the charge on the ion.
- the oxidation number of O is –2 (rule 5) and there are 3 of them so

3(-2)= -6

so N + 3(-2) = -1

N –6 = -1

N = -1 + 6

N = +5

Question- What is the oxidation of Cr in the ion $Cr_2O_7^{2-}$?

Solution –

- The oxidation numbers must add up to –2 as this is the charge on the ion.
- The oxidation number of O is –2 (rule 5) and there are 7 of them so 7(-2) = -14.
- There are 2 Cr also

So 2Cr + 7(-2) = -2
2Cr – 14 = -2
2Cr = -2 + 14
2Cr = +12
Cr = +12/2
Cr = +6

RULE 8 – In <u>neutral molecules</u> the oxidation numbers must add up to <u>zero</u>.

Examples –

Question - What is the oxidation number of S in H_2SO_4 ?

Solution-

- The oxidation numbers must add up to 0 as this is a neutral molecule.
- The oxidation number of H is +1 (rule 6) and there are 2 of them so 2(+1) = +2
- There is no rule for S so we must find this out.
- The oxidation number of O is –2 (rule 5) and there are 4 of them so 4(-2) = -8

So 2(+1) + S +4(-2) = 0
2 + S – 8 = 0
S = - 2 + 8
S = +6

QUESTIONS INVOLVING TRANSITION ELEMENTS

Question - What is the oxidation number of each of the elements in the molecule $FeSO_4$?

Solution –Fe is a transition element and so has a <u>variable valency</u> so in order to work out the oxidation number of Fe in this molecule we must first recognise that the molecule has a sulphate ion (SO_4^{2-}). Seeing as the sulphate ion has an overall charge of –2 then the Fe part of the molecule will have a charge of +2 to balance. As there is only one Fe then the oxidation number of Fe in this molecule is +2.

So

- The oxidation numbers must add up to 0 as this is a neutral molecule.
- The oxidation number of Fe is +2
- There is no rule for S so we must calculate it
- The oxidation number of O is –2 (rule 5) and there are 4 of them so 4(-2) = -8

Then +2 + S + 4(-2) = 0
+2 + S -8 = 0
S = - 2 + 8
S = +6

OXIDATION AND REDUCTION IN TERMS OF OXIDATION NUMBERS

We can now redefine oxidation and reduction in terms of oxidation numbers.

Defn -Oxidation is an increase in oxidation number.

Defn -Reduction is a decrease in oxidation number.

Example –

$$\overset{(0)}{Mg} + \overset{(0)}{Cl_2} \longrightarrow \overset{(+2)\,(-1)}{MgCl_2}$$

We can see that this is an oxidation-reduction reaction (REDOX REACTION) as there is an increase and a decrease on going from the LHS to the RHS of the equation. Mg goes from 0 to +2 and Cl goes from 0 to -1. Mg is oxidised and Cl is reduced. Mg is the reducing agent and Cl_2 is the oxidising agent.

QUESTIONS

Q1. Fill in the blanks in the following paragraph using terms from the following list.
Increase, gain, reducing agent, oxidised, loss, redox, oxidising agent, decrease, reduced.
Oxidation is defined as the ______________ of electrons, while it can also be defined as an ____________ in oxidation number. When a substance gains electrons it is said to be _______________. The substance that looses electrons is called the __________ __________ while the substance that gains the electrons is called the ____________ __________. The term given to reactions in which both oxidation and reduction occurs is a __________ reaction.

Q2. What is the oxidation number of the first mentioned element in the following?
(a) H_2O - H is _____
(b) NaCl - Na is _______
(c) OF_2 - O is _______
(d) CO_2 – C is ________
(e) $K_2Cr_2O_7$ - K is _______
(f) O_3 – O is _______

Sample question - What is the oxidation number of Mn in each of the following
(a) Mn_2O_3
Solution –
- The oxidation number of O is –2
- The sum of the oxidation numbers must be zero as molecule is neutral.
- There are 2 Mn

So 2Mn + 3(-2) = 0
2Mn – 6 = 0
2Mn = +6

Mn = +6/2
Mn = +3

(b) MnO_4^{-}

Solution –

- The oxidation number of O is –2
- The sum of the oxidation numbers must be -1
- There is 1 Mn

So Mn + 4(-2) = -1
Mn – 8 = -1
Mn = -1 + 8
Mn = +7

Sample question - Use oxidation numbers to determine which one of the two reactions, (a) or (b), is a oxidation-reduction reaction. State clearly where oxidation and reduction have taken place.

(a) $Cr_2O_7^{2-} + H_2O \rightarrow 2CrO_4^{2-} + 2H^{+}$

(b) $PCl_5 \rightarrow PCl_3 + Cl_2$

Solution

- Firstly work out the oxidation numbers for each of the elements in the equation
- Secondly look for an increase and decrease in oxidation numbers to see if the equation in an oxidation-reduction equation.
- If there is no change in oxidation numbers on going from the L.H.S. to the R.H.S. of the equation then state that it is not an oxidation-reduction equation.
- If there is a change then pick out the elements that are being oxidised and reduced.

(a) $Cr_2O_7^{2-} + H_2O \rightarrow 2CrO_4^{2-} + 2H^{+}$
(+6)(-2) (+1)(-2) (+6)(-2) (+1)

There is no change in oxidation numbers so this is not an oxidation-reduction reaction.

(b) $PCl_5 \rightarrow PCl_3 + Cl_2$
(+5)(-1) (+3)(-1) (0)

There is a change in oxidation numbers so this is an oxidation-reduction reaction as

P (+5) $\longrightarrow$ P (+3) -a decrease in oxidation number so reduction occurs here

Cl (-1) $\longrightarrow$ Cl (0) -an increase in oxidation number so oxidation occurs here

BALANCING REDOX EQUATIONS USING OXIDATION NUMBERS

Balance the following equation using oxidation numbers

$$MnO_4^- + H^+ + Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O$$

Solution -

- Work out the oxidation numbers of all the elements in the equation

$MnO_4^- + H^+ + Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O$
(+7)(-2) (+1) (-1) (+2) (0) (+1)(-2)

- Identify the elements that show changes in their oxidation numbers

$MnO_4^- + H^+ + Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O$
(+7) (-1) (+2) (0)

- Using only the elements that have changed write this information down mathematically

i.e

Mn(+7) has become Mn(+2) by gaining 5e so it is reduced
Cl(-1) has become Cl(0) by losing 1 e so it is oxidised **however** as there are **2** Cl(0) on the right hand side in the form of Cl**2**, we must double up on the left hand side of the equation so now we have

$Mn(+7) + 5e^- \rightarrow Mn(+2)$
$2Cl(-1) - 2e^- \rightarrow Cl_2(0)$

- We now must get the electrons to balance to get the ratio of oxidising agent to reducing agent.

In this example this means multiplying the top equation by 2 to give a total of 10e lost and multiplying the bottom equation by 5 to give a total of 10e gained. Remember everything in the equation must be multiplied!

$2Mn(+7) + 10e^- \rightarrow 2Mn(+2)$
$10Cl(-1) - 10e^- \rightarrow 5Cl_2(0)$

- we now fill these number ratios into our original equation

$2MnO_4^- + H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 5Cl_2 + H_2O$

- finally we balance all other elements by inspection (hint: leave H until last)

There are 8 O on the L.H.S so there must be 8 O on the R.H.S.

$2MnO_4^- + H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$

There are 16 H on the R.H.S. so there must be 16 on the L.H.S.

$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$

Questions – balance the following equations using oxidation numbers

1. $MnO_4^- + H_2S + H^+ \rightarrow Mn^{2+} + S + H_2O$
2. $Cr_2O_7^{2-} + Cl^- + H^+ \rightarrow Cr^{3+} + H_2O + Cl_2$
3. $ClO_3^- + I^- + H^+ \rightarrow Cl^- + I_2 + H_2O$
4. * $H_2O_2 \rightarrow H_2O + O_2$

SOCIAL AND APPLIED ASPECTS

1. Common household bleaches such as Domestos contain a compound called sodium hypochlorite, NaClO. This substance oxidises dyes in fabrics to become colourless.
2. Chlorine is added to drinking water in small amounts and to swimming pools in larger amounts to oxidise the enzymes in microorganisms to kill them. This disinfects the water and makes it safe to drink or swim in.
3. Hydrogen peroxide is used to oxidise the pigments present in hair to make it blonde.
4. Sulphur dioxide is a reducing agent used in the paper industry to bleach paper.

QUESTIONS FROM EXAM PAPERS

LEAVING CERT 2014

(*c*) Define oxidation in terms of (*i*) electron transfer, (*ii*) change in oxidation number. Use oxidation numbers to identify (*iii*) the oxidising agent, (*iv*) the reducing agent, in the following reaction.

$$Cd + H^+ + NO_3^- \rightarrow Cd^{2+} + NO + H_2O$$

Hence, or otherwise, balance the equation.

LEAVING CERT 2013

The following redox reaction is highly exothermic and is used to produce molten iron for welding pieces of steel together, e.g. sections of railway track:

$$8Al + 3Fe_3O_4 \rightarrow 4Al_2O_3 + 9Fe$$

(*i*) Define *oxidation* in terms of change in oxidation number. Show using oxidation numbers that this is a redox reaction. Identify the reducing agent.

LEAVING CERT 2010

The balanced equation for the oxidation of ethanol to ethanal using sodium dichromate in acidic conditions is as follows:

$$3C_2H_5OH + Na_2Cr_2O_7 + 4H_2SO_4 \rightarrow 3CH_3CHO + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O$$

(*i*) Deduce the oxidation numbers of chromium in the sodium dichromate reagent and in the chromium sulfate product. (7)

LEAVING CERT 2009

Define oxidation in terms of electron transfer. (4)

LEAVING CERT 2008

(a) Define oxidation in terms of (i) electron transfer, (ii) change in oxidation number. (7)

(iii) For the redox reactions shown below, use oxidation numbers to identify the species oxidised in the first reaction and the oxidising reagent in the second reaction. (6)

$$ClO^- + I^- + H^+ \rightarrow Cl^- + I_2 + H_2O$$

$$I_2 + S_2O_3{}^{2-} \rightarrow I^- + S_4O_6{}^{2-}$$

(iv) Using oxidation numbers or otherwise balance both equations. (12)

LEAVING CERT 2007

The halogens are good oxidising agents.

(i) How does the oxidation number of the oxidising agent change during a redox reaction? (4)

(ii) Assign oxidation numbers in each case of the following equations to show clearly that the halogen is the oxidising agent in each case. (12)

$$Br_2 + 2Fe^{2+} \rightarrow 2Br^- + 2Fe^{3+}$$

$$Cl_2 + SO_3{}^{2-} + H_2O \rightarrow Cl^- + SO_4{}^{2-} + H^+$$

Hence or otherwise balance the second equation. (6)

LEAVING CERT 2006

Define oxidation in terms of change in oxidation number. (4)

What is the oxidation number of (i) chlorine in NaClO and (ii) nitrogen in $NO_3{}^-$? (6)

State and explain the oxidation number of oxygen in the compound OF_2. (6)

Using oxidation numbers or otherwise, identify the reducing agent in the reaction between acidified potassium manganate (VII) and potassium iodide solutions represented by the balanced equation below. Use your knowledge of the colours of the reactants and products to predict the colour change you would expect to see if you carried out this reaction (9)

$$2MnO_4{}^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

LEAVING CERT 2005 Q 11

(i) Define oxidation in terms of change in oxidation number. (4)

LEAVING CERT 2004

What is the oxidation number (i) of oxygen in H_2O_2 and (ii) of bromine in $KBrO_3$

LEAVING CERT 2002
Define oxidation number.
Using oxidation numbers, identify which species is being oxidised and which species is being reduced in the following reaction.

$$MnO_4^{-} + Cl^{-} + H^{+} \rightarrow Mn^{2+} + Cl_2 + H_2O$$

Hence or otherwise balance the equation.

MORE QUESTIONS!

1. Define reduction in terms of change in oxidation number.
What is the oxidation number of chromium in $HCrO_4^{-}$?
What is the oxidation number of oxygen in OF_2? Explain why the oxidation number you have given is assigned to oxygen in this case. (Sample paper)

2. Balance the following equation using oxidation numbers:

$$MnO_4^{-} + H^{+} + C_2O_4^{2-} \rightarrow Mn^{2+} + H_2O + CO_2$$

3. Balance the following reaction using oxidation numbers:

$$S_2O_3^{2-} + I_2 \rightarrow I^{-} + S_4O_6^{2-}$$

4. What is the oxidation number of hydrogen in NaH? Explain why you have assigned this oxidation number to hydrogen in this molecule.