

CHEMICAL MONITORING & MANAGEMENT

What is this topic about?

To keep it as simple as possible, (K.I.S.S.) this topic involves the study of:

1. **WHAT CHEMICAL SCIENTISTS DO**
2. **INDUSTRY CASE STUDY: AMMONIA PRODUCTION**
3. **TECHNIQUES IN CHEMICAL ANALYSIS**
4. **ATMOSPHERIC CHEMISTRY & OZONE**
5. **MONITORING & MANAGING WATER SUPPLIES**

...all in the context of Chemistry's importance to our environment and society.

but first, an introduction...

Chemistry's "Bad Press"

Chemical Science has an image problem. Every day, in thousands of locations around the world, Chemical Scientists carry out routine tests to monitor and manage processes that are of vital importance to:

- **Industrial production of important substances we need.**
- **Ensuring that quality & safety standards are met.**
- **Protecting the environment from pollution.**
- **Ensuring that the air we breathe, and our water supplies are clean & healthy.**

Generally, no-one notices all the millions of tests and management decisions that achieve the goals of safety, productivity and efficiency, day-in, day-out.



Photo by Daniel West

However, when something goes wrong and a chemical spill poisons a river, or industrial fumes make people sick,

It's Big News

Sadly, to many people, "Chemistry" is a dirty word!

In this topic, you will firstly look at some of the things that real Chemical Scientists do.

Then you will study one of the most important processes in the Chemical Industry...

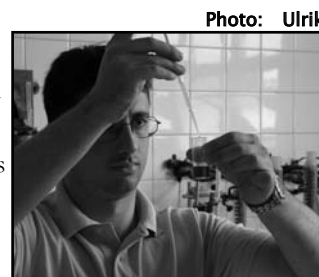
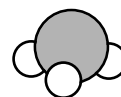


Photo: Ulrik

Production of Ammonia, NH_3



You will study what's good, and what's not good about

OZONE in the air

You will learn more about some of the techniques of

Chemical Analysis

and finally, study aspects of the management of your community's

Water Supply System

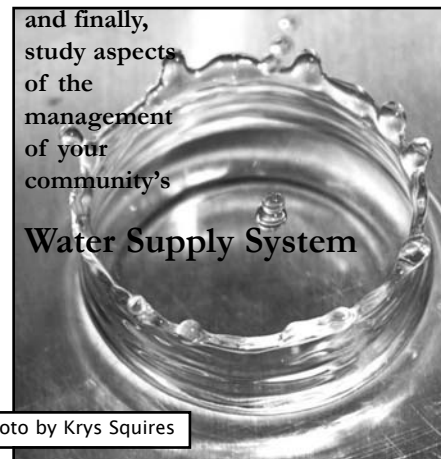
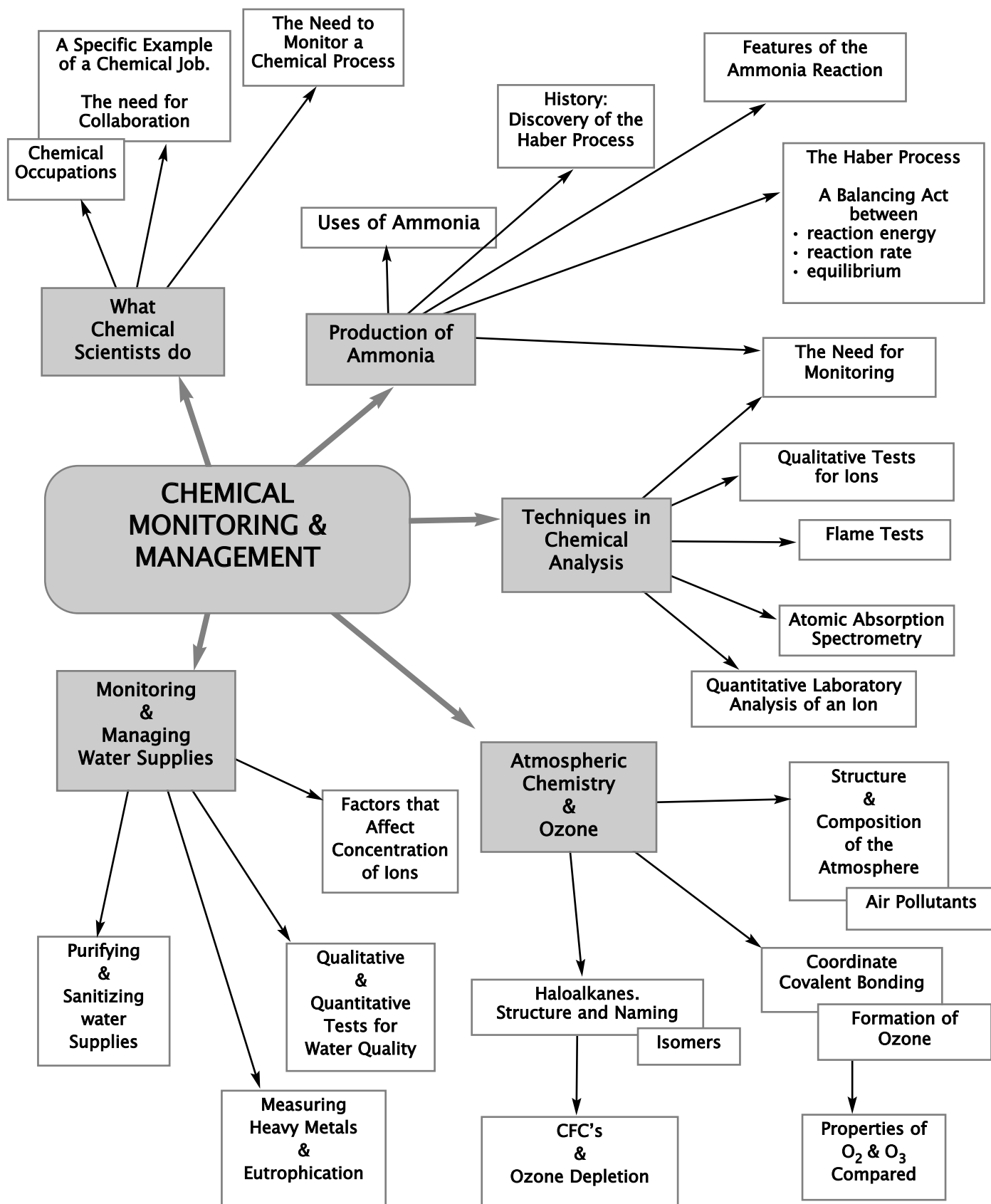


Photo by Krys Squires

CONCEPT DIAGRAM (“Mind Map”) OF TOPIC

Some students find that memorizing the OUTLINE of a topic helps them learn and remember the concepts and important facts. As you proceed through the topic, come back to this page regularly to see how each bit fits the whole. At the end of the notes you will find a blank version of this “Mind Map” to practise on.



1. WHAT CHEMICAL SCIENTISTS DO

The Variety of Chemical Occupations

Since every substance in the Universe is a chemical, then every human endeavour which deals with substances will, sooner or later, use the services of a Chemical Scientist.

Chemists may be involved in:

- soil, water or air analysis
- developing new materials, or managing production in
 - chemical industry
 - pharmaceuticals
 - foods
 - agricultural products
 - metals
 - fuels
 - plastics... and many more.
- criminal investigation
- pollution and corrosion control
- materials for electronics and electro-chemical industries
- environmental science and protection
- quality assurance, in a wide range of industries

Specific Duties of a Laboratory Toxicologist

The UK-based company Altrix provides drug-testing services to Government and corporate employers who need to screen (for example) job applicants for evidence of drug abuse or certain diseases, such as hepatitis.

The company has developed a detection method, based on a non-invasive mouth-swab or hair sample, which can identify a wide range of drugs of abuse, such as cocaine or cannabis. Their laboratory uses high-tech methods of Chemical Analysis, such as gas chromatography and mass spectrometry.

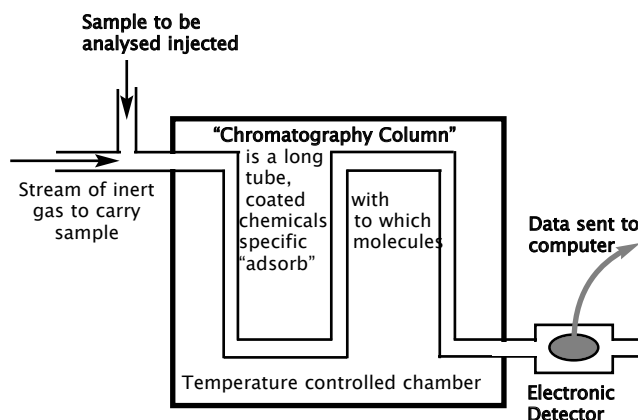


The company employs Chemical Scientists to carry out all the technical and scientific aspects of the operation.

As well as carrying out the chemical analyses, the scientists report the results back to the clients, and need to be prepared to appear as “expert witnesses” should any matter end in a legal challenge.

The Principle of Gas Chromatography

The sample to be analysed is vaporized and injected into a stream of inert “carrier” gas such as helium.



As the mixture flows through the “Chromatography Column” different molecules adsorb to the coating according to the polarity, shape and size of each molecule. Each substance keeps moving through the column, but at different rates, so each “fraction” emerges separately and is picked up by a sensitive detector.

In the case of drug-screening, the detector is sensitive to the minute amounts of residues and metabolic products that remain in the body for months after using heroine, cocaine, cannabis, etc.

The Need for Collaboration

The image of the solitary, mad-genius Scientist working in his (they’re always male!) secret laboratory to make brilliant-but-misguided breakthroughs, began with the “Frankenstein” story 200 years ago, and persists still.

This image couldn’t be further from the truth. Real Science is a team effort, and real Scientists must co-operate, communicate and collaborate with their colleagues and clients.

For example, a Laboratory Toxicologist employed by Altrix would need to

- compare analysis results from other tests done by other workers, to confirm the validity of a client’s screening.
- discuss results and conclusions with other professionals.
- collaborate on the usage of equipment, the scheduling of tests to be completed and the deadlines for completion.
- keep up to date with new developments in the field, by communicating with other scientists and attending seminars and conferences.

The Need to Monitor a Chemical Process

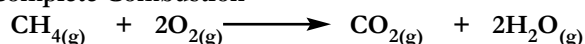
Many chemical processes are very sensitive to any change in the conditions of the reaction involved.

For example, most reactions will run at a different rate if the temperature changes. A change in pressure could cause an equilibrium to shift, according to Le Chatelier's Principle, and affect the yield of a reaction.

As a specific example, consider the effect of oxygen availability on a combustion reaction, such as the burning of natural gas, which is mostly methane gas:

If there is a good supply of oxygen, and the reactants mix well, the products are carbon dioxide and water vapour.

Complete Combustion

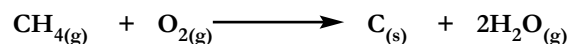
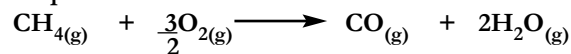


This combustion reaction could be part of an industrial process such as:

- heating a furnace or kiln for making bricks or ceramics.
- or
- boiling water for steam supply to an industrial complex.

However, if there is a shortage of oxygen, the products can include carbon monoxide, or even carbon (soot).

Incomplete Combustion



Incomplete combustion is undesirable because:

- less energy is released per unit of fuel used.
- carbon monoxide is toxic.
- soot can build up in equipment, causing problems.

In any industrial application, it is vital to ensure efficient, economical operation without emission of toxic fumes, or extra maintenance problems caused by incomplete combustion.

To manage this process, it would be important that someone (e.g. a Chemical Engineer) monitors the combustion by regularly

- measuring the flow, and mixing of fuel and air.
- measuring the temperature within the combustion area.
- measuring the composition of the exhaust gases.

**Practical, Applied Chemistry
is all about
Monitoring & Management**

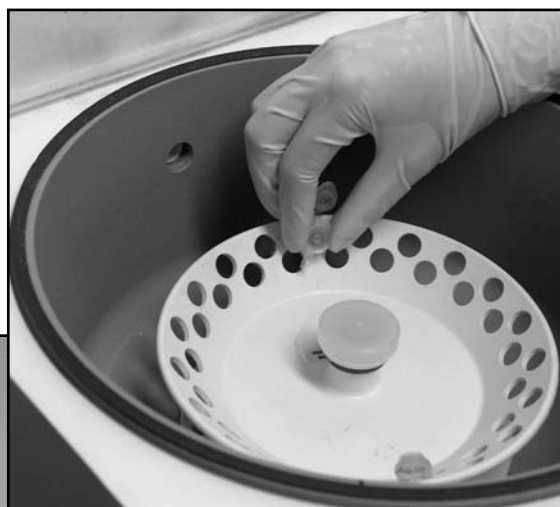


Photo by Dain Hubley



Photo by Nick Fletcher

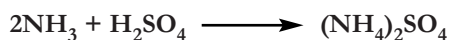
2. INDUSTRIAL CASE STUDY: AMMONIA PRODUCTION

The Uses of Ammonia

Ammonia, NH_3 , is one of the most important industrial chemicals in the world. Its production is measured in millions of tonnes, and its uses are very widespread, including the manufacture of:

- fertilizers (urea and ammonium compounds)
- nitric acid, which in turn is used in the manufacture of
 - explosives
 - dyes and pigments
 - fibres and plastics
- household cleaners and detergents

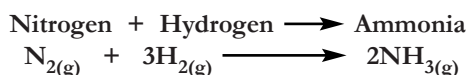
For example, to make the common fertilizer “sulfate of ammonia”, ammonia is reacted with sulfuric acid in a simple acid-base reaction:



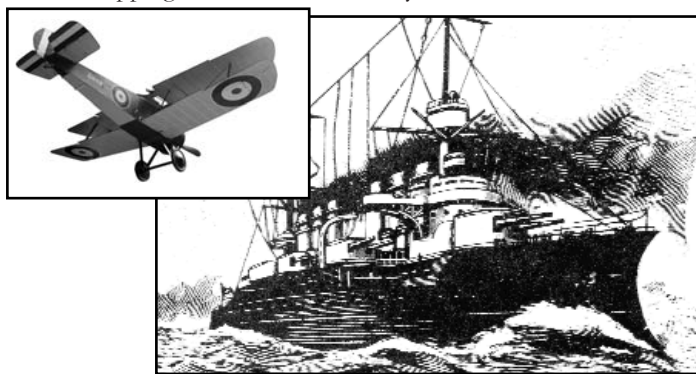
History: Development of Ammonia Synthesis

Prior to World War I, the manufacture of fertilizers and explosives was largely dependant on the supply of “saltpetre” (sodium nitrate) from natural deposits in Chile.

In 1908, the German Chemist Fritz Haber, developed a method to make ammonia from its elements, nitrogen and hydrogen, using an iron catalyst. Later, Carl Bosch developed the process to an industrial scale.



Since nitrogen makes up about 80% of air, and hydrogen can be obtained from hydrocarbons in petroleum, this process did away with the dependance on mining and shipping from a distant country.



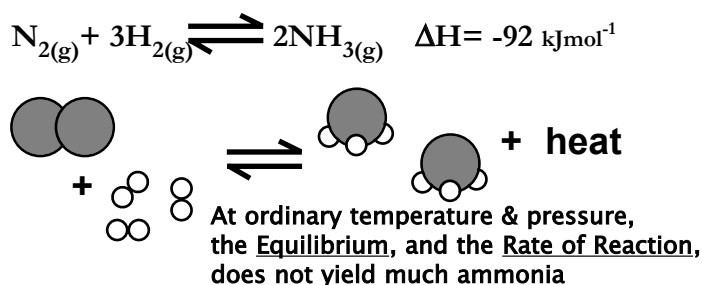
This was a hugely significant development at that time. Europe was on the brink of war, with explosives and food supplies (needing fertilizers) about to become critically important.

Shipping from Chile could be stopped by the enemy, but the Haber-Bosch process allowed Germany to be self-sufficient in fertilizers and explosives made from ammonia.

Industrial Production of Ammonia by the Haber Process

Almost 100 years after it was developed, the manufacture of ammonia by the Haber process is one of the most important industrial chemical processes in the world.

The reaction is not an easy one: it is exothermic, but at ordinary temperatures the reaction is painfully slow, and the equilibrium lies well to the left, with a very low yield of ammonia.



Speeding Up A Reaction

You learnt in an earlier topic that the rate of any reaction depends on the reactant molecules colliding with enough energy (“activation energy”) to start the process of breaking old bonds and making new ones.

Basically, there are 3 ways to increase the rate of reaction:

Increase the Temperature

At higher temperatures the molecules move faster. They collide more often and with more energy.

Increase the Concentration of Reactants

If the concentration is higher, the “density” of molecules is higher and so the chance of a collision is more. More collisions gives a higher reaction rate.

In gases, increasing the pressure increases the concentration of molecules by forcing them closer together.

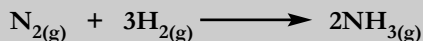
Using a Catalyst

Catalysts have the effect of reducing the activation energy of the reaction. At any given temperature, a catalyst makes it more likely that colliding molecules will have enough energy to react, so the rate increases.

Fritz Haber was an educated Chemist... he knew all these things. His discovery of the process which bears his name was no accident, but the result of applying chemical knowledge to solve the problem of supply that his country, and the world, faced in the early 20th century.

The Haber Process Explained

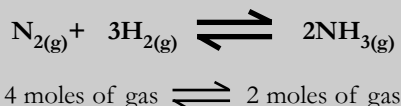
For maximum efficiency, the reactant gases are mixed in the MOLE RATIO of the balanced equation



Mixture of H_2 & N_2
(in ratio 3:1)
pumped in under
pressure of
300 atmospheres

High Pressure

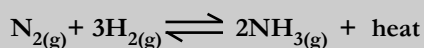
causes the equilibrium to shift right
increasing the yield of ammonia



By Le Chatelier's Principle,
increasing the pressure causes
the equilibrium to shift right, in an
attempt to create less gas
and a lower pressure.

The reaction is exothermic,
so heat is produced constantly

Since the reaction is **Exothermic**



by Le Chatelier's Principle
lower temperatures would
drive the equilibrium right,
and increase the yield of ammonia

The Need to Monitor

The Haber process is based on a delicate balancing act between reaction energy, reaction rate and equilibrium. It needs constant monitoring of

- the ratio of reactant gases.
- temperature & pressure (each affects the other) which must be optimal to ensure efficiency and yield.
- levels of contaminating gases (such as carbon monoxide and sulfur compounds) which could "poison" the catalyst.

Constantly removing Ammonia
from the mixture causes the
equilibrium to shift to the right,
which increases the yield

Gases out of reaction
chamber are a mixture of
ammonia, plus
unreacted
 H_2 & N_2

Coolant out

Condenser
Ammonia
liquifies

Coolant in

Liquid
Ammonia
out

Unreacted H_2 & N_2
re-pressurized
and
returned to
reaction vessel

Incoming gases partially pre-heated by the heat from reaction

Catalyst
granules in
reaction
chamber

Heater
Unit
Temp
400°C

REACTION VESSEL

The use of a catalyst
lowers the activation energy,
and increases reaction rate.

The catalyst used is the iron ore
"Magnetite" (Fe_3O_4) with its surface
reduced to a layer of elemental iron.

The catalyst achieves the desired rate
of reaction at a lower, more
economical temperature.

BUT...

The higher the temperature, the
FASTER the **RATE** of reaction.
SO...

400°C is a COMPROMISE

Worksheet 1

1. List 6 industries which rely on the services of Chemical Scientists.

.....

2. As an example of a specific job, list 3 duties of a Laboratory Toxicologist.

.....

3. Explain the basic scientific principle of chemical analysis using the technique of Gas Chromatography.

.....

4. List 3 reasons why a Laboratory Toxicologist would need to collaborate with his/her colleagues.

.....

5. With reference to a combustion reaction in an industrial setting:

a) explain how the reaction conditions can affect the products of the reaction.

.....

b) Explain the need for monitoring the reaction, and list 2 factors which might be monitored.

.....

Worksheet 2

Fill in the Blank Spaces

Ammonia is used in the manufacture of a).....
 for agriculture, and for b)..... acid. This, in turn,
 is used to manufacture c).....,
 and

Until the early 20th century, manufacturing these things
 depended on the supply of d).....
 mined in natural deposits in e)..... In 1908,
 Fritz f)..... developed a method to make
 ammonia from g)..... and
 This was enormously significant for Germany which could
 continued making h)..... and
 during World War I.

The reaction to make Ammonia is not an easy one. At room
 temperature and pressure, the reaction rate is very
 i)....., and the equilibrium lies well to the
 j)....., favouring the k).....

l)..... temperatures increase the reaction rate,
 but also shift the equilibrium to the m).....,
 because the reaction is n).....-thermic.

The modern production of ammonia by the o).....
 Process is a balancing act between reaction energy, reaction
 p)..... and the q)....., to achieve
 efficient and economical production. The reactant gases are
 mixed in the ratio 3 parts r)..... to 1 part
 s)..... and combined at a pressure of
 t)..... atmospheres. This high pressure forces the
 equilibrium to the u).....

The reaction mixture is heated to approximately v).....
 °C. This temperature is a compromise between increased
 w)..... and the x).....,
 which shifts left at higher temperatures.

A catalyst of y)..... lowers the
 z)..... energy and speeds up the rate. This
 allows a aa)....., more economical
 temperature to be used.

The reaction mixture flows out of the reaction chamber to
 a ab)..... where ammonia is
 ac)..... Unreacted hydrogen & nitrogen are
 ad).....

To ensure efficient production, monitoring of the reaction
 mixture ratio, ae)..... and
 is required. The presence of contaminating gases (such as
 af)..... and)
 is important too, since these could ag).....
 the catalyst, if allowed to build up.

3. TECHNIQUES IN CHEMICAL ANALYSIS

Chemical Analysis

One of the key processes in Chemical Monitoring and Management is the analysis of samples to detect and/or measure the levels of a chemical of interest.

In this section, you will study some examples of chemical analysis, at 2 different levels:

Qualitative Analysis

identifies a chemical species, but does not measure quantity.

Quantitative Analysis

measures the amount or concentration of a chemical.

The syllabus requires that you study techniques to detect and/or measure 9 specific ions. There are many other ions and compounds that need monitoring in industry or in the environment.

The Need to Monitor Levels of Some Ions

There are certain human activities which can release dangerous or harmful ions into the environment. Monitoring the levels of these in air, water, soil or food is essential to help protect people, and the environment, from harm.

Two important examples are:

Phosphate Ions

Phosphate ions (PO_4^{3-}) are a normal and healthy part of the natural environment at normal concentrations.

However, human activities can increase the levels of phosphate ion in water environments. This leads to **Eutrophication**; a process where water plants and algae are “over-fertilized” and grow excessively. This clogs waterways, and leads to masses of dead, rotting algae which takes all oxygen from the water... ecosystem dead!

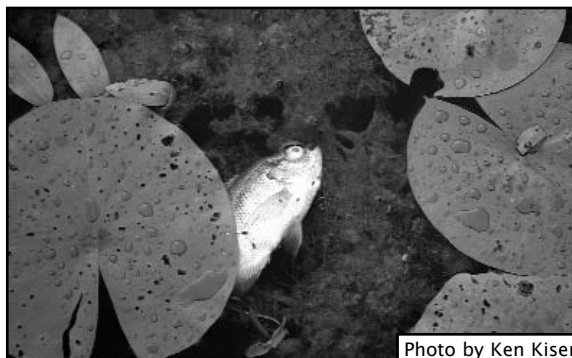


Photo by Ken Kiser

The human activities responsible are mainly agricultural fertilizer run-off from farmland, and discharge of human sewerage into waterways. Taking water for irrigation also reduces water flow and makes the problem more likely.

Lead Ions

Lead is a toxic “heavy metal” which is not present in the natural environment in significant amounts. Even very low levels are dangerous because it can accumulate in the body until it reaches toxic levels.

Lead poisoning in an adult leads to chronic neurological disease. In children it can cause permanent brain damage.

In the past, lead compounds were included in a variety of products including house paints (banned years ago) and “super” petrol (now phased out and replaced by ULP... “unleaded petrol”). These changes were made specifically to reduce the lead levels in the environment.



Photo by Pam Roth

Perhaps the main concerns about lead are fading now that leaded-petrol is no longer pumping lead-laden fumes into the air, but lead persists in the environment for centuries, so monitoring of previously polluted areas is still needed.

It is also necessary to monitor for lead emissions from industries which produce or use lead, such as lead smelters, or car battery manufacturers.

The ions specified by the syllabus are

CATIONS (+)

Barium
Calcium
Lead
Copper
Iron

ANIONS (-)

Phosphate
Sulfate
Carbonate
Chloride

Qualitative Identification of Ions

The simplest laboratory methods for detecting and identifying the ions being studied, are to use Precipitation Reactions and Flame Tests.

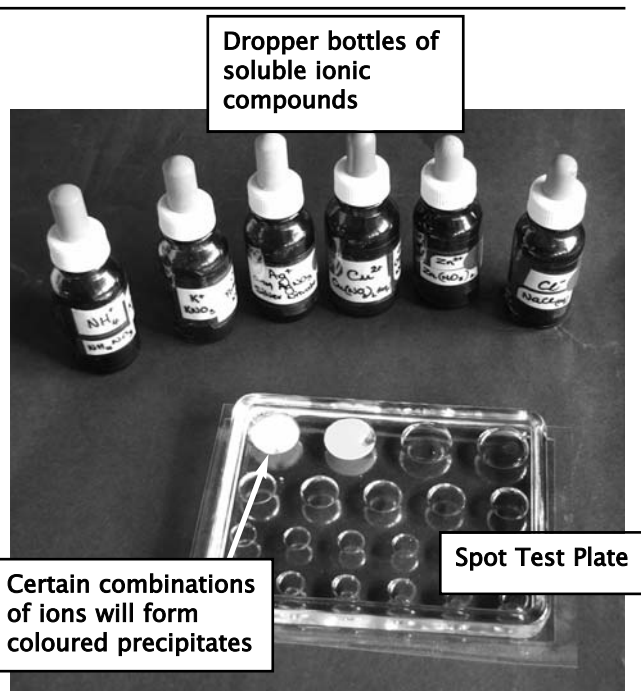
You will have done a series of laboratory exercises to firstly, familiarize yourself with the tests themselves, and then to use the tests to identify some “unknown” samples.

Precipitation Reactions

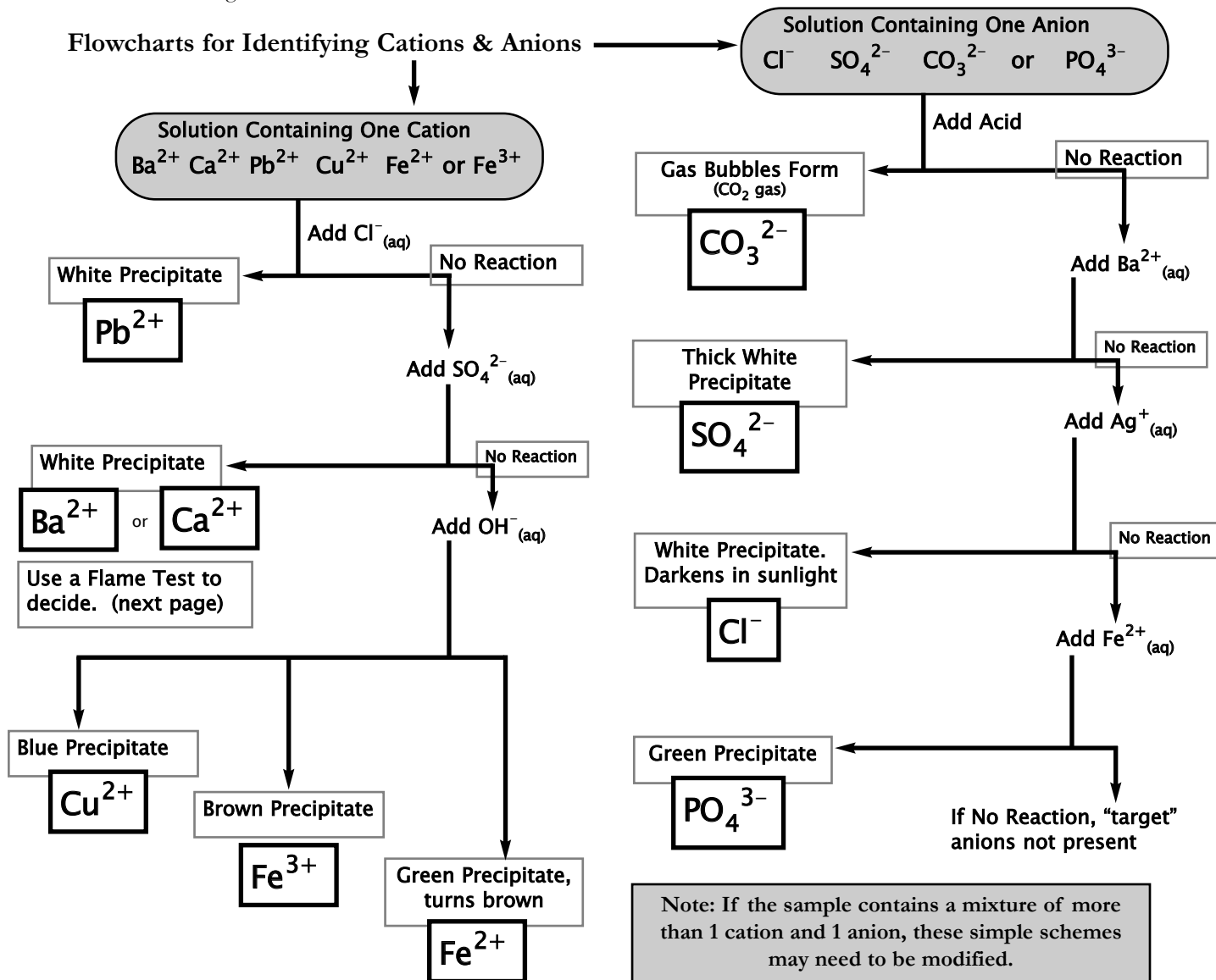
You were introduced to these in the Preliminary Topic, “Water”.

Most ionic compounds are soluble in water, but some have extremely low solubility. If certain combinations of cation and anion are mixed together in a solution, they may form an insoluble solid and precipitate from solution.

You previously studied these reactions to learn about the “Solubility Rules”. A knowledge of these “rules”, and of the common precipitate colours can now be used to test a solution containing “unknown” ions.

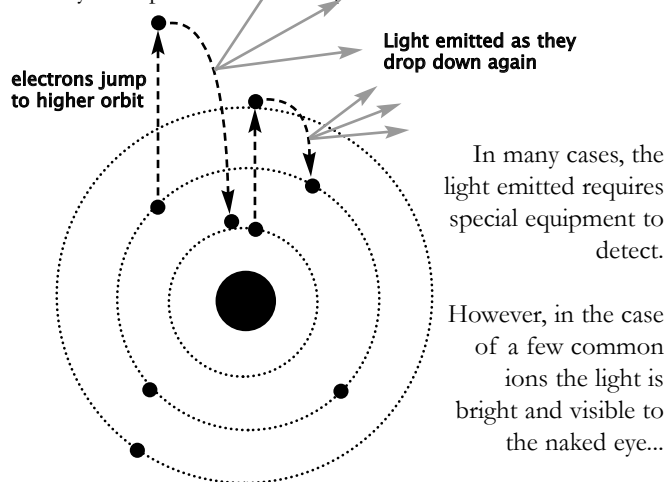


Flowcharts for Identifying Cations & Anions



Flame Tests

When atoms absorb energy, electrons may “jump” up to a higher energy level (a higher, unoccupied orbit). Usually, they will immediately drop down to a lower level again, and in the process they lose the excess energy by emitting light rays at a precise set of frequencies.



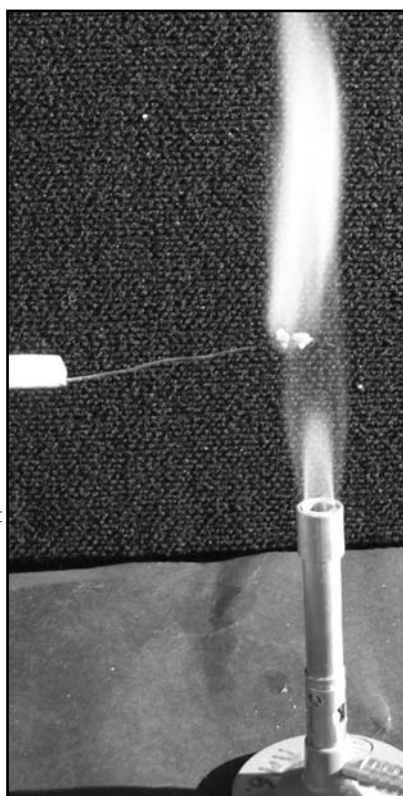
...this can be used for identification.

In the flowchart on the previous page, the ions Ca^{2+} and Ba^{2+} both gave the same results for precipitation reactions.

They can be easily distinguished if a sample of each solution is “flamed” in a bunsen.

Each one “flares” briefly with a distinct and characteristic colour.

Of the ions in our list to be studied, 3 give flame test colours that are useful for analysis.



Flame Test Colours

Ion	Flare Colour
Barium	lime green
Calcium	orange-red
Copper	blue

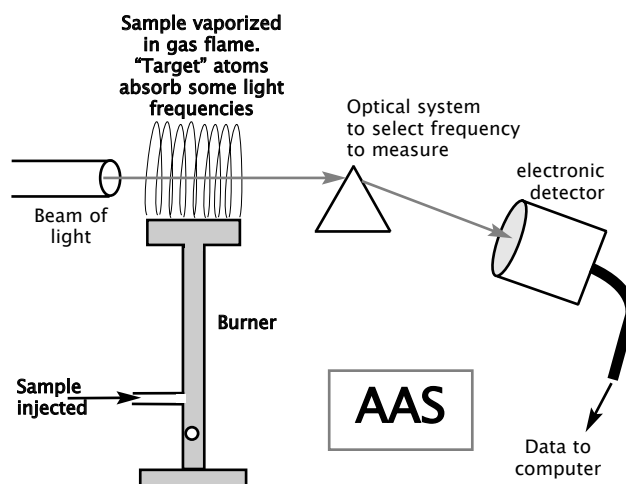
As you will see next, the principle involved here, can be used for **quantitative analysis** as well...

Atomic Absorption Spectroscopy (AAS)

When a small sample of atoms are energised so they emit light, as shown at the left, the amount of light emitted is too small for measuring the amount or concentration.

However, the exact frequencies of light that a particular type of atom will emit, are also the same frequencies that that atom will absorb strongly, and this time it is more easily measured.

AAS is a technique of beaming light through a vapourized sample, and measuring the amount of the light (of the appropriate frequencies for the “target” atoms) that is absorbed. The amount of light absorbed is in direct proportion to the amount of “target” atoms present, so it measures them quantitatively.



Each type of atom has its own unique set of absorption frequencies (see next page), so AAS can positively identify each atom, and measure its concentration accurately.

The process was invented and developed in Australia in the 1950's and is sensitive to extremely low concentrations of atoms, mainly metals. It has become very important for chemical analysis of “trace elements” in soil or water.

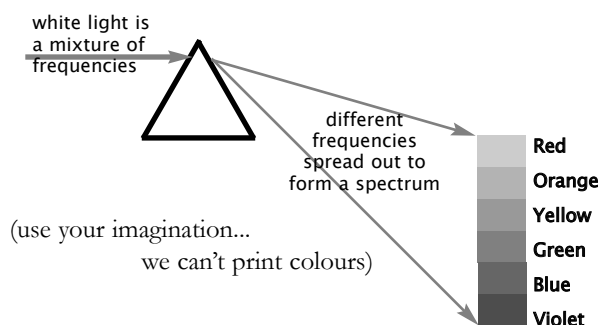
When substances are present in extremely low concentrations they are often measured in units of “parts per million” (ppm). For example, if there was one atom of Radon gas for every million atoms in the air, its concentration would be 1 ppm.

AAS can routinely measure concentrations of over 60 elements at levels of only 0.01 ppm and less.

The technique of AAS has revolutionised the study of “trace” elements and their effects.
Examples next page.

Emission & Absorption Spectra

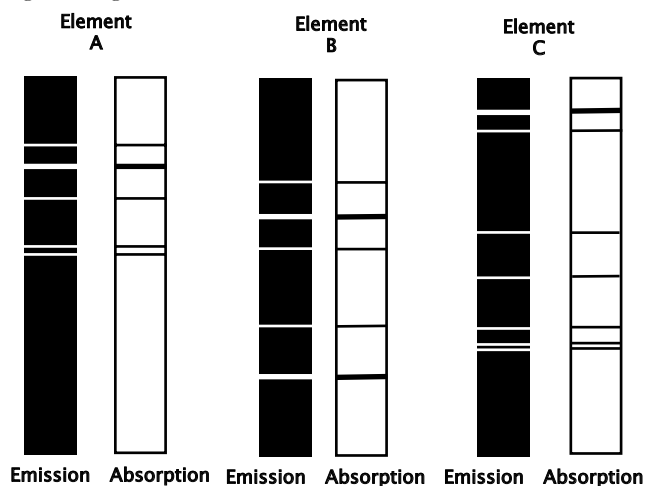
You should be familiar with the idea of a “spectrum” of light. For example, if “white” light is passed through a prism, the different frequencies are separated, and the familiar rainbow colours appear.



If the light emitted by atoms of a particular element is put through a prism, the spectrum shows very narrow bright lines on a dark background, because only certain frequencies are given out. The pattern of lines is characteristic for each element.

If the same element absorbs light it will be at exactly the same characteristic frequencies. The spectrum will have dark lines on a bright background.

The following diagram shows 3 fictitious elements, just to give the general idea.



In AAS, the optical system allows the measurement of absorption of light of specific frequencies which correspond to the spectrum of a particular element.

The amount of this light absorbed by a sample is in direct proportion to the concentration of that type of atom.

By measuring the absorption of light of known concentration standard solutions a “calibration graph” can be constructed. When the absorption of the same frequencies by test samples has been measured, the concentration of the target element can be read from the calibration graph. (example at right)

Examples of the Use of AAS

The value of AAS lies in its ability to measure quantities of elements that are too low to be detected by the “normal” laboratory chemical analyses.

Essential Trace Elements in Soil

A famous case occurred in Western Australia in the 1950-60's. In one region of the state many sheep farmers found their animals were chronically unhealthy, despite apparently good pastures and disease control.

Using the newly developed technique of AAS, the CSIRO found that the soil (and then the plants and the sheep) were lacking tiny amounts of the element cobalt.



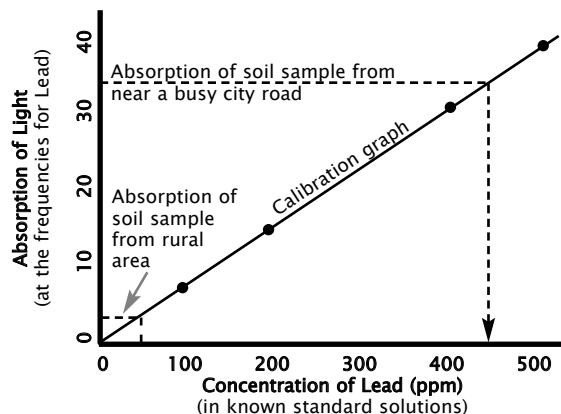
Photo: Guy Halpe

Further study revealed that all mammals need “trace” amounts of cobalt for one particular, important enzyme in their cells. In the cobalt-poor area the sheep were unhealthy because they could not make the vital enzyme.

Once this was understood, the sheep were given a slow-release cobalt “pill”, and a multi-million dollar industry was rescued from trouble.

Monitoring Lead Pollution

AAS is ideal for measuring extremely small levels of pollutant chemicals, such as lead, in (say) the soil. By measuring the absorption of light (at lead's frequencies) by AAS, the sort of data discovered was:



It was data like this, from AAS analysis, that was important in the decision to stop using leaded petrol, since it revealed the amount of lead pollution occurring in heavy-traffic areas.

AAS data is vital for monitoring pollutants like lead.

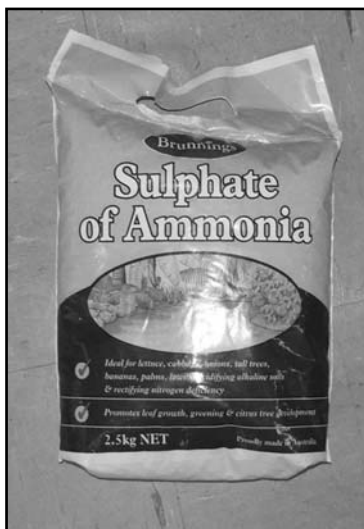
A Quantitative Laboratory Analysis

You will have carried out a practical analysis to measure the sulfate content of a lawn fertilizer.

A product commonly tested is shown.

The simplest method to use is **Gravimetric Analysis** (collect a solid and weigh it) following an ionic precipitation reaction.

As covered earlier, sulfate ions can be identified (and in this case collected quantitatively) by precipitation using Ba^{2+} ions.



An outline of a typical procedure (and example results and analysis) is at the right.

Below is a discussion of some of the commonly encountered difficulties with this analysis.

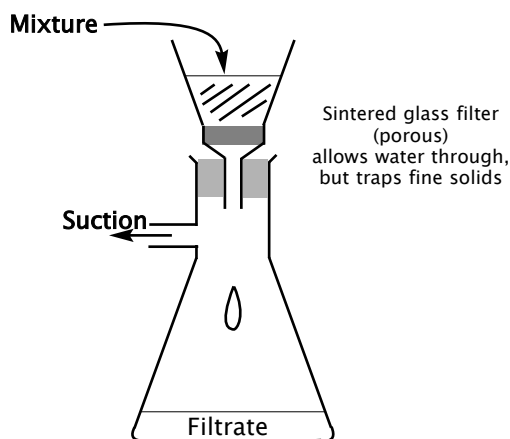
Reliability of the Results

The “reliability” of any analysis can be assessed by how close (or otherwise) the results are when the procedure is repeated. In a class situation, a number of different groups usually carry out the same analysis. If the various group results are in close agreement, then the procedure can be considered “reliable”.

Common Difficulties

The major problem with this analysis is that the BaSO_4 precipitate is notoriously difficult to collect by ordinary filtration, because it is very fine-grained and a lot gets through the filter paper.

It is better to use a sintered glass crucible & vacuum filter.

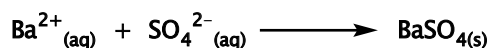


Accurately Weigh
a Sample of Fertilizer
(approx 2 grams is suitable)

Dissolve in about 100mL
dilute HCl

Filter to remove
any insoluble material

Slowly add
an excess of Ba^{2+}
and stir well
(about 40mL of 0.5 mol L^{-1}
 $\text{BaCl}_{2(\text{aq})}$ is suitable)



Filter to collect solid barium
sulfate

Don't forget to dry
and pre-weigh the
filter paper, and to
rinse the residue
with pure water.

Dry the residue in an oven
and weigh

Typical Results and Analysis

Mass of fertilizer sample = 2.34 g

Mass of dried precipitate (BaSO_4) collected = 2.67 g

moles of BaSO_4 : $n = m/\text{MM}$ $\text{MM} = 233.4$
 $= 2.67/233.4$
 $= 0.01144 \text{ mol}$

\therefore moles of sulfate = 0.01144 mol (ratio 1:1)

mass of sulfate: $m = n \times \text{MM}$ $\text{MM}(\text{SO}_4) = 96.1$
 $= 0.01144 \times 96.1$
 $= 1.10 \text{ g}$

\therefore % sulfate in sample = $\frac{1.10}{2.34} \times 100 = 47.0\%$

Worksheet 3

Part A Fill in the Blank Spaces

Qualitative Analysis means to a)..... a chemical species. To analyse quantitatively means to b).....

Some human activities release dangerous ions (or harmful amounts) into the environment. For example, phosphate ions can cause the process of c)..... to occur in water environments. This is when there is d)..... Later, the dead, rotting vegetation e)..... from the water. The main sources of extra phosphate are f)..... and

Lead ions can g)..... in the body and cause h)..... in children. Until recently, the main source of lead pollution was from the use of i).....

The simplest qualitative tests to identify ions is to use j)..... reactions and k)..... tests.

A simple scheme to identify the 6 syllabus cations is:

1. Add l)..... ion. A white precipitate indicates the presence of m).....
2. Add n)..... ion. A white precipitate indicates either o)..... or
- These can be differentiated by a p).....
3. Add q)..... ion. A blue precipitate indicates r)..... while a brown precipitate indicates s)....., and a green precipitate (which slowly goes brown) indicates t).....

To identify the 4 syllabus anions:

1. Add u)..... If carbonate ions are present you will see v).....
2. Next, add w)..... ion. If sulfate ions are present you will see x).....
3. Add y)..... ion. A white precipitate (which darkens in sunlight) indicates z).....
4. Finally, add aa)..... ion. A green precipitate indicates ab).....

Of the 6 syllabus cations, 3 give distinctive colours in a flame test: barium flares ac)....., calcium flares ad)..... and copper flares ae).....

AAS stands for af).....
This technique is able to quantitatively measure extremely small concentrations of an element. Basically, it works by measuring the amount of ag)..... absorbed by atoms in a vaporized sample. Each element has its own unique absorption ah)..... The AAS equipment is able to select the ai)..... of light which correspond to the aj)..... spectrum of the element being analysed.

AAS has made it possible to study “ak).....” elements which could not be previously analysed. In a famous case, AAS analysis solved a major problem in a sheep-farming area by detecting a deficiency of al)..... which was making the sheep sick. AAS also makes it possible to monitor pollutants such as am)....., which is dangerous even at low levels in the environment.

Part B Practice Problems

1. Identifying Ions

Each of the following describes a series of tests carried out on an “unknown” ionic solution. Name the ion(s) identified in each case.

- a)
 - added acid: no reaction
 - Added Ba ion: no reaction
 - added Ag ion: white precipitate
- b)
 - added Cl ion: no reaction
 - added sulfate ion: white precipitate
 - flame test flared orange-red colour
- c)
 - added Cl ion: no reaction
 - added sulfate ion: no reaction
 - added hydroxide: green precip., went brown
- d)
 - added acid: bubbles formed
- e)
 - added acid: no reaction
 - Added Ba ion: no reaction
 - added Ag ion: no reaction
 - added Fe^{2+} ion: green precipitate
- f)
 - added Cl ion: no reaction
 - added sulfate ion: no reaction
 - added hydroxide: blue precipitate

2. Quantitative Analysis of Sulfate Ion

Two different lawn fertilizers were analysed gravimetrically by dissolving a sample in dilute hydrochloric acid, adding excess Ba^{2+} ion, then collecting the BaSO_4 precipitate, drying and weighing.

Fertilizer A: sample mass = 4.46g
mass of BaSO_4 collected = 3.27g

Fertilizer B: sample mass = 1.93g
mass of BaSO_4 collected = 2.66g

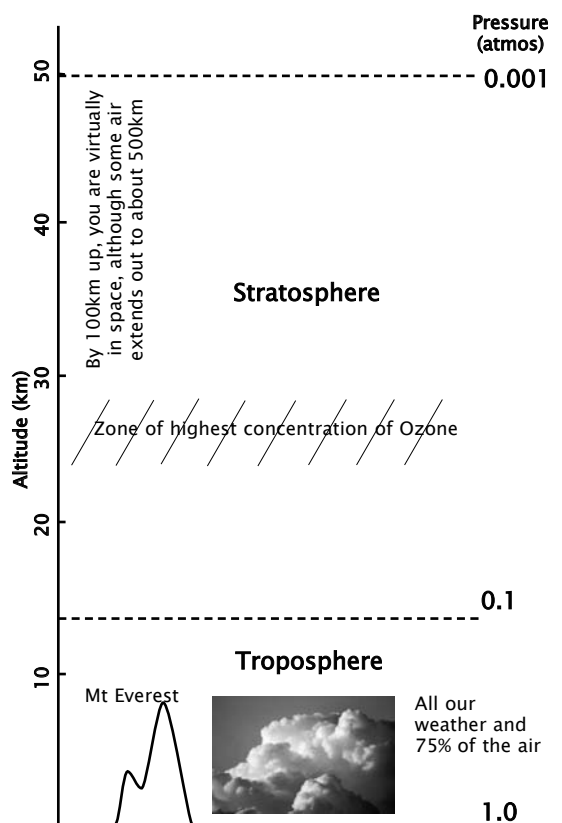
Calculate the % by mass of sulfate in each fertilizer.

**WHEN COMPLETED, WORKSHEETS
BECOME SECTION SUMMARIES**

4. ATMOSPHERIC CHEMISTRY & OZONE

Structure of the Atmosphere

The atmosphere is composed of a number of layers, although these different layers cannot be seen. The air within each layer rarely crosses the boundary to the next layer (i.e. each is more or less a separate body of gas) and each layer has certain differences in temperature profile and chemistry. It is only the lowest 2 layers you need to know about.



Composition of the Atmosphere

Water vapour in the air varies from about 0.5 - 5%, but all the other gases of the air are remarkably constant:

Nitrogen	78.1%	% of dry air
Oxygen	20.9%	
Argon	0.9%	
	99.9%	

Another dozen or more gases make up the remaining 0.1%. Their concentrations are best measured in parts per million (ppm). The most significant are:

Carbon dioxide	350	ppm	(and rising!)
Inert gases	≅ 30	ppm	
Methane	1-2	ppm	

OZONE	0.02	ppm (at ground level)
	up to ≅ 8	ppm (in stratosphere)

Air Pollutant Chemicals

One of the main indicators of human economic and technological development over the last 200 years or so, is the release into the atmosphere of a range of substances which are

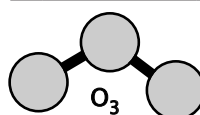
- toxic
- and/or • environmentally damaging.

Pollutant	Human Activities Responsible
Carbon monoxide CO	Incomplete combustion in vehicle engines, fires.
Sulfur dioxide SO ₂	Fossil fuels (S impurities burn). Smelting of sulfide ores.
Hydrocarbons C _n H _m	Unburnt fuels, solvents, spills.
"NO _x gases" NO & NO ₂	High-temp. combustions in engines & power stations.
Particulates dust, ash, smoke	Combustions, e.g. burning-off, agriculture, mining.
Ozone, O ₃	Photochemical smog.

More About Ozone

Way back in Preliminary Topic 1, you were introduced to the concept of "Allotropes"; different forms of the same element, such as graphite and diamond, the allotropes of carbon.

Ozone is an allotrope of oxygen.



up high : good!
down low : bad!



Always good!

- Ozone in the lower atmosphere is a toxic pollutant. At concentrations as low as 0.2 ppm it causes lung damage, and aggravates other breathing problems. For people who have asthma, for example, ozone is a life-threatening substance.

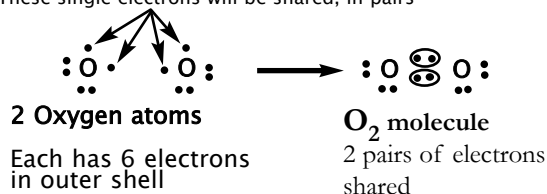
- Ozone in the upper atmosphere is an important shield against dangerous U.V. radiation from the Sun. In the Stratosphere, where ozone concentrations are as high as about 8 ppm, up to 90% of the damaging UV is absorbed by ozone molecules.

Ironically, human activities produce ozone in the Troposphere and destroy ozone in the Stratosphere!

Coordinate Chemical Bonding

You are already familiar with “normal” covalent bonding, and you should be able to describe the O_2 molecule using Lewis (“electron-dot”) formulas.

These single electrons will be shared, in pairs

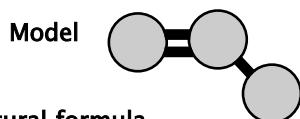
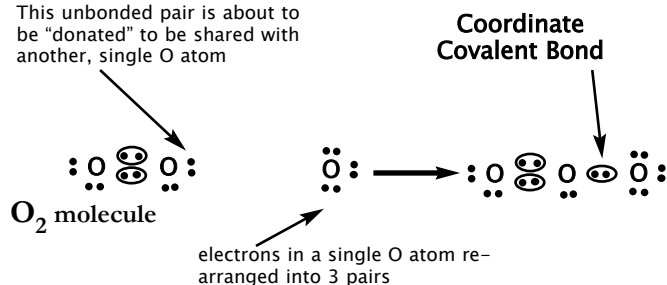


Structural formula



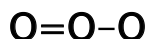
To form an ozone molecule, another oxygen atom must bond to the O_2 , and the way this occurs is an example of a “Coordinate Covalent Bond”...

This unbonded pair is about to be “donated” to be shared with another, single O atom



The O_3 molecule is bent, due to the electron pairs all getting as far away from each other as possible

Structural formula



A Coordinate Covalent Bond forms when both the shared electrons come from the same atom

Once a coordinate covalent bond has formed, it is indistinguishable from a “normal” covalent bond.

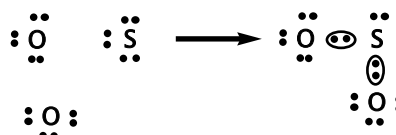
Other Examples

of Coordinate Covalent Bonding

You can now understand the formation of some chemical species which previously couldn't be explained.

Sulfur Dioxide, SO_2

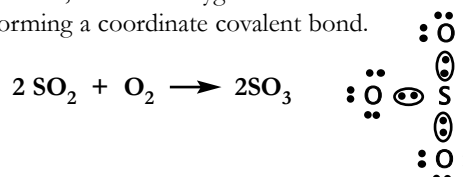
Sulfur atom & 2 oxygen atoms, with all electrons in pairs



The sulfur atom supplies all the electrons to share in these coordinate covalent bonds

Sulfur Trioxide, SO_3

Notice in the Lewis formula for SO_2 , the sulfur atom still has another unshared pair of electrons available. Under the right conditions, another oxygen atom can bond there, again by forming a coordinate covalent bond.

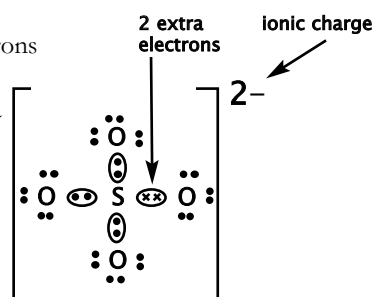


The Sulfate Polyatomic Ion, SO_4^{2-}

Notice that in SO_3 the sulfur atom has just 6 electrons in the outer shell. The “rule of 8” is not always obeyed.

But, what if 2 extra electrons were added?

(They might come from a metal atom, for example.) There is room for them in the sulfur atom's orbit, and then they can be shared with a 4th oxygen atom.



All the polyatomic ions are formed in a similar way, and many covalent compounds involve coordinate covalent bonds. (That's why it can be difficult to predict formulas for covalent compounds)

Properties of O_2 and O_3 Compared

Like all allotropes, O_2 and ozone show quite different properties. For example:

Property	O_2	O_3
boiling point ($^{\circ}C$)	-183	-111
density of liquid (g/cm^3)	1.2	1.6
smell	odourless	strong
chemical reactivity	reactive (e.g. combustion)	highly reactive
chemical stability	stable molecule	highly unstable

It is the chemical properties that are of most significance.

Explaining the Differences

The properties are the result of structure and bonding.

The differences in physical properties are due simply to the O_3 molecule being larger and heavier, which increases the dispersion forces between molecules.

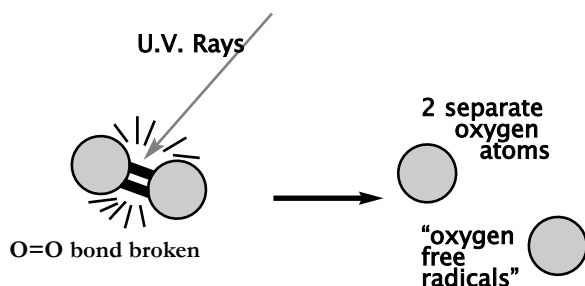
The $O=O$ double bond in O_2 is quite strong. It requires almost 500 kJ of energy per mole of bonds, to break. In contrast, it only takes about 100 kJ/mole to break one of the bonds in O_3 . This is why ozone is unstable and very highly reactive... the molecule's bonds are more readily broken, so the activation energy for any reaction is quite low, and ozone readily enters oxidation reactions.

Oxygen free-radicals

How can an ozone molecule be formed in the first place?

Up in the high Stratosphere, conditions are very different to down here at the bottom of the atmosphere. It's cold, the air pressure is extremely low and there is a lot of high energy radiation from the Sun.

Oxygen doesn't absorb U.V. radiation very much, but occasionally a U.V. ray scores a direct hit and smashes the molecule into 2 separate oxygen atoms. These are called "oxygen free-radicals".

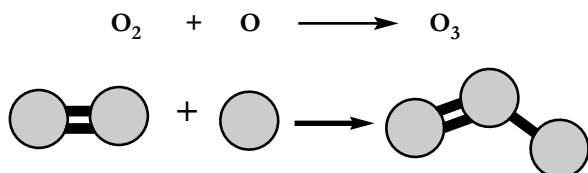


Oxygen free-radicals are even more highly reactive than ozone, but what is there to react with in the high atmosphere?

The most common substances up there are:

- nitrogen, (N₂) which is very stable and unreactive.
- oxygen molecules, (O₂) which are fairly reactive.
- argon, (Ar) which is totally inert.

So, the free-radical atoms tend to react with oxygen molecules:



This is how ozone is formed in the upper atmosphere. Although it is unstable and highly reactive, there is virtually nothing up there for it to react with, and the air of the Stratosphere hardly mixes with the Troposphere, so it builds up to a concentration of up to about 8 ppm.

It's interesting to note, that the U.V. rays which create the oxygen free-radicals and thus create ozone, are strongly absorbed by the ozone. Less than 10% of the dangerous, incoming U.V. penetrates to the surface, thanks to ozone.

Chemical Reactivity Comparison

Oxygen O ₂	Ozone O ₃	O free-radical
Chemically Active	VERY active	Extremely Active

Depletion of the Ozone Layer

For over 100 years, scientists have been sending high-altitude balloons up into the Stratosphere to collect information and air samples, so the presence of ozone has been known for many years, and its role as a U.V. shield has been recognised since the 1920's.

How Ozone Levels are Measured

• Automatic chemical analysis units are sent aloft in high altitude balloons. Direct chemical measurements of ozone concentration can be collected at any desired altitude.

• The "Dobson Spectrophotometer" is a ground based instrument (invented 1925) which measures the amount of several different frequencies of U.V. light reaching the surface.

By comparing the level of a U.V. frequency known not to be absorbed by ozone, with a frequency that is strongly absorbed by ozone, a calculation gives the amount of ozone in the "total column" of air above the instrument.

• Similar instruments are carried by satellites in orbit. They measure the UV scattered from different layers of the atmosphere, and so can measure a "profile" of ozone concentrations at different altitudes.

The Evidence for Ozone Depletion

Regular measurements of ozone concentration have been made since 1925, and intensive measuring has been going on since the 1970's.

A world wide decline in Stratospheric ozone levels of about 10% has been recorded. More importantly, it has been found that every spring over Antarctica, a "hole" develops in the ozone layer. A vast area of the Stratosphere temporarily loses up to 90% of its ozone for several months each year. The size of this "hole" varies, but some years it expands to come very close to populated areas.

So What?

The problem with ozone depletion is that (for example) a 30% decrease in ozone concentration would mean a 50% increase in the level of dangerous U.V. radiation reaching ground level.

U.V. radiation is known to cause sunburn, eye damage and increased incidence of deadly skin cancers in humans. Plant studies indicate that large increases in U.V. could seriously disrupt crop growth, possibly leading to a food supply crisis.

Before learning about how ozone is being destroyed, you need to know about another type of carbon compound...

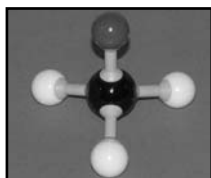
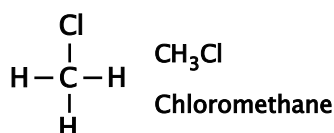
the **Haloalkanes**.

Haloalkanes

“Halo-” refers to the “Halogens”... the general name for the elements of group 7 of the Periodic Table; fluorine, chlorine, bromine and iodine.

Haloalkanes are alkane molecules in which one or more hydrogen atoms have been replaced by halogen atoms.

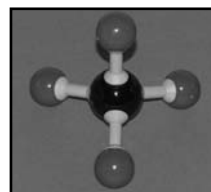
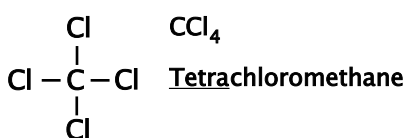
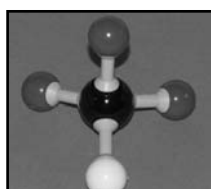
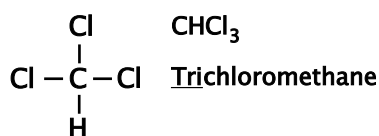
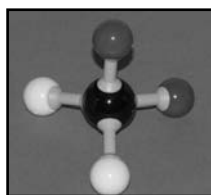
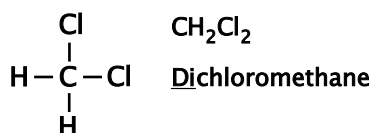
The simplest example is a methane molecule with one of its hydrogens replaced by (say) a chlorine atom.



If, instead of chlorine, the replacement atom was:

- fluorine... CH_3F = fluoromethane.
- bromine... CH_3Br = bromomethane.
- iodine... CH_3I = iodomethane.

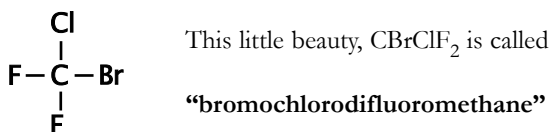
What if 2, or more, hydrogens were replaced by chlorine atoms?



Prefixes to use for the number of halogen atoms:

1 = no prefix	4 = tetra
2 = di	5 = penta
3 = tri	6 = hexa

What if there is more than one type of halogen atom substituted? **They must be ordered alphabetically by halogen name...** (not by any prefixes used, though).

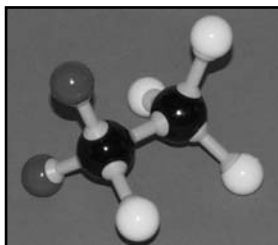


Isomers

When the molecule gets bigger, another variation that can occur is in the position of the various atoms.

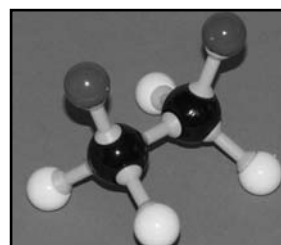
For example, these 2 molecules are ethane, with 2 chlorines substituted for hydrogens.

Both Cl atoms attached to same carbon.



1,1-dichloroethane

Cl atoms attached to different carbon atoms.



1,2-dichloroethane

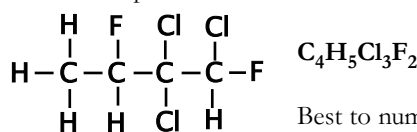
These molecules have the same molecular formula ($\text{C}_2\text{H}_4\text{Cl}_2$) but have a different structure, and are different compounds. Their m.p. & b.p., density, and other properties would be slightly different. We must give them a different name.

This is done by numbering the carbon atoms (from whichever end gives the smallest result) and stating the position number for every halogen atom present.

ISOMERS

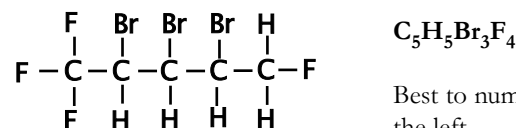
have the same molecular formula,
but different structures.
They are different compounds,
with different properties.

More Examples:



Best to number the carbons from the right.

1,2,2-trichloro-1,3-difluorobutane



Best to number from the left.

2,3,4-tribromo-1,1,1,5-tetrafluoropentane

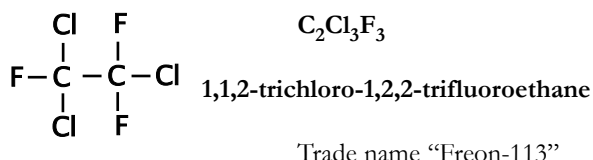
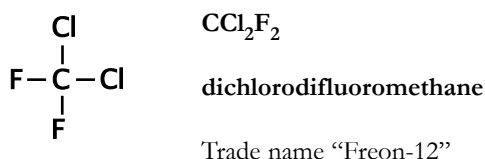
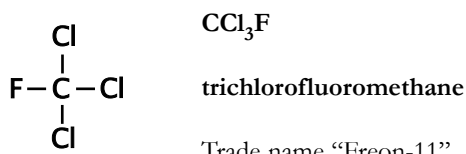
Try the **WORKSHEET** at the end of section

The Chlorofluorocarbons (CFC's)

One particular class of haloalkanes have become notorious as ozone destroyers... the "CFC's".

CFC stands for "chlorofluorocarbon". These are alkane molecules in which ALL the hydrogens have been replaced by chlorine and fluorine atoms.

Three of the most used CFC's were:



These compounds (in general):

- have boiling points near room temperature.
- are very stable, and chemically unreactive and inert.
- are non-toxic, non-inflammable and non-corrosive. (i.e. very safe)

This set of properties made the CFC's ideal to use for:

- the "working fluid" in refrigerators.
- propellant gas in aerosol cans.
- the gas to "blow up" foam plastics.
- small fire extinguishers, cleaning sprays and solvents.

From about the 1930's, CFC's began to be widely used, reaching a peak in the 1970's. The methods of usage meant that the CFC's were eventually released into the atmosphere.

Although the air of the Troposphere does not mix with the Stratosphere much, the CFC's released have gradually diffused into the upper atmosphere. This might take 20 years, but these chemicals are very stable and easily last that long.

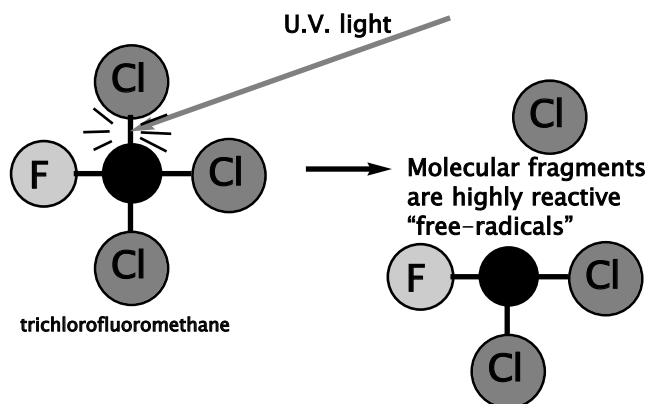
Once there, we now know that they cause a series of reactions which destroys ozone.

By international agreement, production and use of CFC's is now banned. However, all the millions of tonnes released back in the 1950-70's is still up there, doing its thing...

What CFC's Do to Ozone

Remember how ozone is formed? The first step is the production of an "oxygen free-radical" when U.V. strikes an oxygen molecule.

A similar thing can happen to a CFC molecule:



A likely product of this is a **chlorine free-radical**; a loose atom of chlorine, which is even more reactive than an oxygen free-radical. We use the symbol "Cl•"

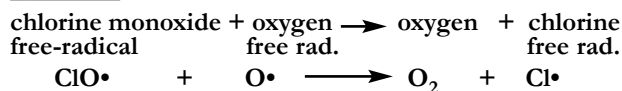
What happens next:

Reaction 1

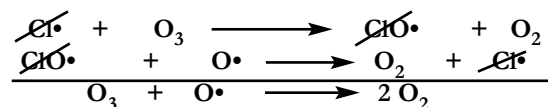


Meanwhile, the U.V. has just busted an oxygen atom and formed an oxygen free-radical too. Normally this might make another ozone molecule, but if the ClO• radical finds it first:

Reaction 2



If you add reactions 1 and 2 together, several species "cancel out":



The "net equation" shows that overall, ozone has been converted to oxygen, and the oxygen free-radicals (which potentially could have formed more ozone) have been "mopped up".

Notice also, that the Cl• free-radical is regenerated by reaction 2, and can do it all over again...
it is acting as a catalyst.

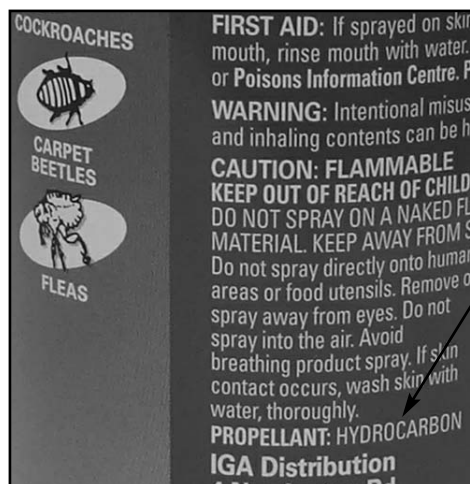
A little CFC can destroy a lot of ozone.

What's Been Done About CFC's?

CFC's are also potent "Greenhouse gases", although their contribution to Global Warming is minor compared to their impact on the ozone layer.

Between 1987-1994 a series of international agreements have banned the manufacture and use of CFC's, although some developing countries have been given a little more time to comply.

CFC's have been replaced by:



Hydrocarbons, for example, as propellants in aerosol cans. Hydrocarbons are inflammable, so this is less safe than using CFC's, but saves ozone.



Can the Ozone Layer Recover?

The answer is yes. Although CFC's are very stable, they cannot last forever, and once their concentration begins to fall, the normal ozone production in the Stratosphere will restore the normal balance.

The CFC's released back in the 1970's are still reaching the Stratosphere, and so ozone depletion is serious. However, this should peak in the next 10-20 years and then the recovery will begin. It is estimated that ozone levels will be back to normal in 50-100 years.

In the meantime, governments must:

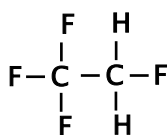
- continue to comply with, and enforce the ban on CFC's, and maintain pressure on other nations to comply.
- educate people about the dangers of U.V. and the ways to protect themselves from it.
- financially support the continued monitoring of ozone concentrations.

HFC's are hydrofluorocarbons, containing hydrogen, fluorine and carbon, but no chlorine. These are being used in refrigeration, foam plastics, etc. HFC's are more expensive, and slightly less efficient than CFC's.

However, HFC's mostly decompose in the Troposphere, and if any does reach the Stratosphere it is "ozone-friendly" because it contains no chlorine.

The main HFC being used in Australia is

1,1,1,2-tetrafluoroethane, $C_2H_2F_4$



Worksheet 4

Part A Fill in the Blank Spaces

The lowest layer of the atmosphere is the a)..... Above that, extending up to about 50km, is the b)..... The air consists of the 3 main gases, c)....., and which combined make up d).....%.

Significant pollutants in the atmosphere include

- e)..... (CO) from incomplete combustion
- sulfur dioxide, from f).....
- “NO_x” gases from g)..... and
- ozone, formed in petrochemical “h).....”

At ground level, ozone is a dangerous pollutant which can cause i)..... However, up in the Stratosphere, ozone is very important because it absorbs j).....

Ozone forms by “k)..... covalent bonding”, which is when both the electrons being shared l)..... All the “m)..... ions”, and many covalent compounds are formed by this type of bonding.

O₂ and O₃ are n)..... of oxygen. They have quite different properties, but it is their o)..... properties which are most significant. Compared to O₂, ozone is much more p)..... because the molecule is quite q)..... While the bonds in O₂ require about 500 kJ/mol to break, the bonds in O₃ need only about r)..... kJ/mol.

Ozone forms in the upper atmosphere when U.V. radiation strikes an s)..... molecule and splits it into 2 t)..... These are extremely reactive, and can react with an O₂ molecule to form u).....

The concentration of ozone can be measured by sending up analysis devices in balloons, or by using a v)..... This measures different frequencies of w)..... and from this, the amount of ozone can be calculated. Measurements made over the past 80 years reveal that, since the 1970's, ozone levels have declined about x).....% generally, but that a huge “y).....” forms temporarily over z)..... every spring. Potentially, even partial destruction of the ozone layer can result in increased exposure to U.V., leading to aa)..... and increased There is also a potential for disrupted plant growth, leading to ab).....

“Haloalkanes” are ac)..... molecules in which one or more hydrogen atoms have been replaced by atoms of ad)....., or which collectively known as the ae).....

A type of haloalkane, the af)..... (CFC's) are believed to be responsible for ozone depletion in the Stratosphere. CFC's were widely used for ag)....., but have now been banned. CFC molecules released at ground level gradually make their way up into the Stratosphere. If struck by U.V. radiation, a ah)..... free-radical can be formed. This can act as ai)..... in a series of reactions which turn ozone into aj).....

CFC's have now been replaced by hydrocarbons and ak)..... These are not as efficient, but are “ozone-friendly”. The ozone layer is expected to continue to degrade for some years, but then slowly recover within about al)..... years.

Part B Practice Problems

1. Co-ordinate Covalent Bonding

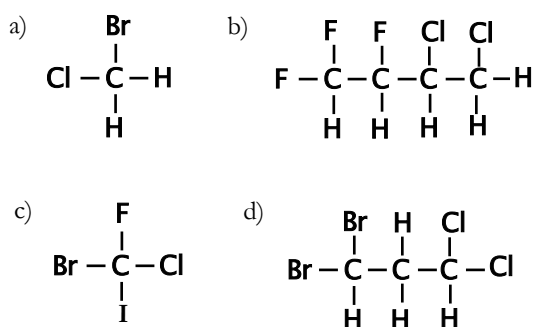
a) Construct a Lewis Formula for carbon, with its 4 electrons in pairs. Add an extra pair. Now attach 3 oxygen atoms in coordinate covalent bonds. Write a formula, and name, for the polyatomic ion.

b) As above, but begin with nitrogen (5 electrons). Add 1 extra electron, then 3 oxygens by coordinate covalent bonding. Formula and name?

c) Construct a Lewis Formula for a water molecule. Now add a hydrogen ion (H⁺) so it forms a coordinate covalent bond with the oxygen atom. Formula and name?

2. Naming Haloalkanes

Name each of the following compounds.



3. Isomers

a) Draw structural formulas for 3 different isomers of trichloropropane. Name each correctly.

b) Draw structural formulas for 4 different isomers of bromochlorobutane. Name each correctly.

5. MONITORING & MANAGING WATER SUPPLIES

Measuring Water Quality

One of the most fundamental requirements of any community is to have a supply of healthy drinking water.

More than that, our communities expect that the water will not only be safe, but will taste good, look crystal clear, will not clog pipes with mineral deposits, will allow soap to lather-up readily, and will make a really nice cup of tea!

To ensure that the water supply is of high quality requires constant monitoring and measurement of such qualities as:

Turbidity

This is a measurement of “cloudiness” or lack of clarity. Turbidity is related to the presence of suspended solids.

Total Dissolved Solids (TDS)

This measures the solids dissolved in the water.

Concentration of Common Ions

While the TDS measures all dissolved solids, it is also possible to measure particular common ions. For example, measuring chloride ion (Cl^-) is a simple way to assess the level of salt (NaCl) present.

Hardness

“Hard” water has significant amounts of Ca^{2+} and Mg^{2+} ions dissolved. These cause mineral deposits to build up inside water pipes (eventually blocking them and requiring expensive replacement) and also interfere with the lathering of soap.

Acidity

Pure water has a $\text{pH} = 7$, but normal good quality drinking water is often slightly below that (e.g. $\text{pH} = 6.5$) due to the natural dissolving of CO_2 . Polluted water can have values more than 2 pH units either above or below neutrality.

Dissolved Oxygen

& Biological Oxygen Demand (BOD)

This measurement is the most important measurement for assessing safety of the water for drinking. Low oxygen levels mean the water is “stagnant”. This might be safe to drink, but usually tastes unpleasant, so is not acceptable.

BOD measures whether the dissolved oxygen changes over time in a sealed container. If it does, this is a strong indication of living things present and growing, in the water. This is very dangerous to the community since the micro-organisms could be disease-causing pathogens.

Practical Work: Qualitative & Quantitative Water Tests

Turbidity measuring tube

You may have carried out a series of analyses on water samples, to experience making some of the assessments described above. Typically, you might have tested

- your local tap water) for
- samples of sea water) comparison
- samples from a creek or bore)

Total Dissolved Solids

Traditionally, this is measured by evaporating a water sample in a pre-weighed evaporating dish, and weighing the residue. You may have done this with a sea water sample and measured about 3 grams of salt per litre.

However, tap water has so little TDS ($< 0.1\text{g/L}$) that it is difficult to measure by evaporation.

Another way is shown. This probe actually measures electrical conductivity, but this relates to TDS because the dissolved solids are usually ionic, and increase the conductivity of the water.



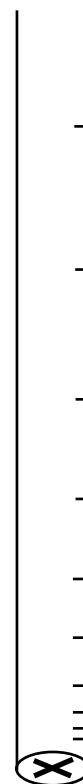
Turbidity

This is usually measured by the depth of water required before a highly visible mark becomes invisible. You may have used a device similar to the diagram. As you look down the tube at the cross drawn on the bottom, water is slowly poured in at the top.

Dirty creek water will obscure the cross within a few centimetres.

With good quality tap water the cross may still be visible when the tube is nearly full.

The tube is marked with a measuring scale, but the numbers don't relate to any chemical measurement and really are for comparison only.

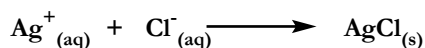


More Water Tests Next Page...

Qualitative & Quantitative Water Tests (continued)

Concentration of Common Ions

The same precipitation reactions learnt earlier can be used qualitatively to detect specific ions. For example, if chloride ion is present, the addition of silver nitrate solution will cause:



The solid silver chloride causes a visible “cloudiness” (turbidity).

Using a sample of sea water you could collect the solid by filtration, and measure it by gravimetric analysis.

In tap water there is usually such a small quantity that quantitative measurement by weighing a precipitate would be difficult, but you might have done a “semi-quantitative” estimation as follows:

Silver chloride is not totally insoluble, so in very dilute solutions (like tap water) the “cloudiness” depends on concentration. If you have dilute solutions of silver nitrate (0.01 mol L^{-1} and $0.0001 \text{ mol L}^{-1}$) and add one drop to certain volumes of water samples, whether or not a visible “cloudiness” appears gives an estimate of chloride ion concentration.

For example:

	Goes cloudy	Not cloudy
• 1 drop 0.01 mol L^{-1} in 10 mL sample	> 0.2	< 0.2

(values are mg/L of Cl^- ion, approx.)

• 1 drop $0.0001 \text{ mol L}^{-1}$ in 100 mL sample	> 200	< 200
---	-------	-------

Water Hardness

To measure Ca^{2+} and Mg^{2+} ions quantitatively requires a complicated titration involving the reagent “EDTA”.



A simple, qualitative test is to place shaved soap pieces in a bottle with some water and shake vigorously.

“Hard” water (try sea water) will hardly foam at all, and may form a “scum” on the surface.

“Soft” water will foam-up .

For comparison tests, be sure to keep the experiment “fair” by using exactly the same quantities of soap, water and shaking.

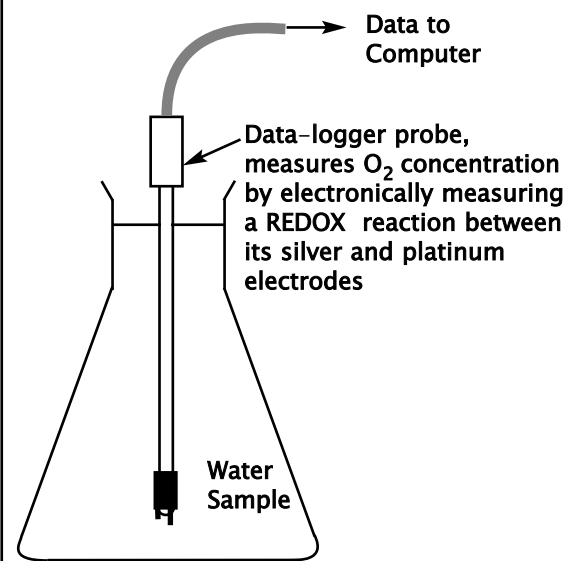
Acidity

Use “pH paper” (Universal indicator) and a colour comparison chart, or use a pH meter.

It is vital that any glassware used is perfectly clean and preferably rinsed with water from the source about to be tested.



Dissolved O_2 and BOD



Using the equipment shown, instantaneous readings of dissolved oxygen levels can be obtained.

To measure **BOD**, 2 samples are needed.

- one is measured immediately, and value recorded.
- the other must be kept in a sealed container (with no air bubbles) in the dark (so algae cannot grow) for 5 days, then measured again.

If the reading is lower than the original, it means that something has used up the oxygen in the water sample.

This could indicate not only the presence of live microbes in the water, but also that there must be organic matter for them to feed on...

This indicates polluted water!

Factors That Affect the Concentration of Ions in Waterways

All our water supplies originally fell as rain or snow. When this hit the ground it was virtually pure water, but by the time it reaches the river or lake it may have picked up a variety of dissolved ions. Which ones, and at what concentration depends on factors such as:

- **Pathway.** If the rainwater flows across the surface of natural bush and forest it will dissolve only small amounts of Na^+ , Cl^- , SO_4^{2-} , etc ions.

If it flows into and through underground aquifers it may dissolve much more material (higher TDS), including ions like Ca^{2+} and Fe^{3+} . Ground water is often very “hard”.

- **Type of soil and rock** the water flows through.
- **pH of the water.** Generally, the more acidic (lower pH) the water, the more ions it will dissolve.
- **the nature of human activities in the catchment.** Water which drains from agricultural land may dissolve ions from farm fertilizers and animal dung, such as phosphate and nitrate ions.

Water flowing through a garbage dump could pick up ions of heavy metals (e.g. lead, mercury from old batteries).

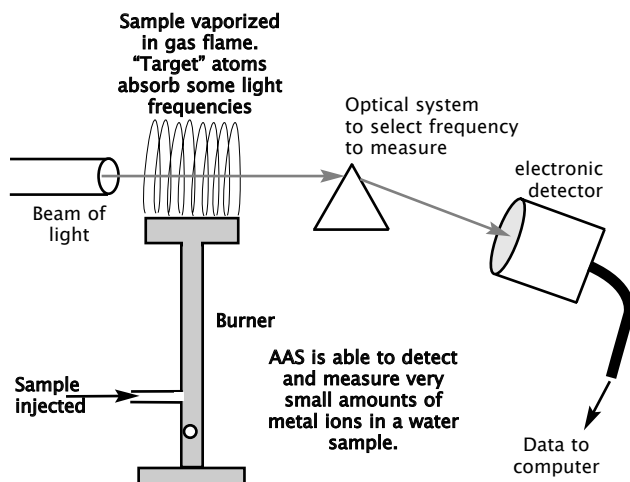
Human activities might actually discharge extra ions into the water catchment, such as phosphates and nitrates from sewerage treatment works, or heavy metal ions from factories, mines, and storage dumps.

Heavy Metal Pollution of Water

Of all the possible ions that might end up in our water, the heavy metals like lead and mercury are the most dangerous to human health.

To detect and monitor these ions in water, gravimetric analysis using precipitation reactions will not work, because these metals are dangerous at levels too low to be detected and analysed gravimetrically.

A suitable method has already been discussed earlier in this topic... **Atomic Absorption Spectroscopy (AAS)**



Monitoring Eutrophication of Waterways

The process of “Eutrophication” was described briefly earlier in this topic.

Nitrate and phosphate ion concentrations in water can rise when:

- water flows through farm land and picks up fertilizers.
- treated sewerage is discharged into waterways.

These ions act as fertilizers for water plants and algae, leading to over-growth. This can clog streams with water plants and produce “algal blooms” of toxic algae. Later, as the mass of plant material dies, the rotting process absorbs oxygen from the water (i.e. BOD becomes extreme) and aquatic animal life may suffocate.

Quite apart from ecological damage, water from streams with eutrophication is quite unsuitable for human consumption, due to the high load of microbes present.

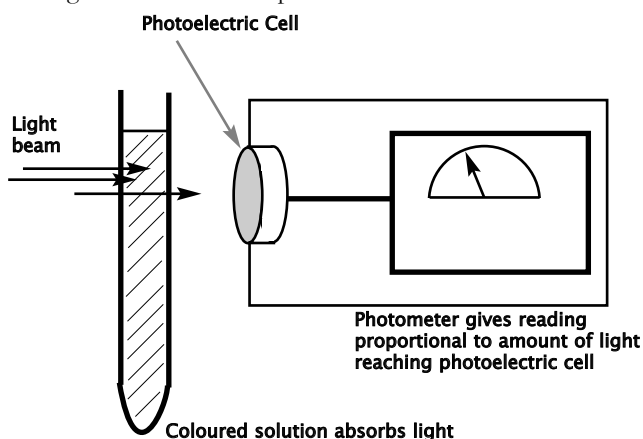
Potential Eutrophication problems can be predicted by measuring the phosphate concentration of the water. Once again, the simple precipitation/gravimetric tests learnt earlier are not sensitive enough.

Measuring Phosphate Ion by Photometry

One way to measure phosphate levels is to react a water sample with the reagent **ammonium molybdate** ($(\text{NH}_4)_2\text{MoO}_4$), then add ascorbic acid (vitamin C).

A reaction occurs with phosphate ions which forms an intense blue-coloured solution.

The more phosphate present, the deeper the blue colour. This is measured by a photometer, a simple device which electronically measures the amount of light which passes through the solution to a photoelectric cell detector.



Known concentration PO_4^{3-} solutions are used as “standards” and reacted and measured the same way to produce a “calibration graph”. The concentration of the “unknown” sample is read from the graph according to how much light passes through it.

Purifying and Sanitizing Water Supplies

The best way to survive a car accident is to drive carefully so as not to have one, and the best way to purify and sanitize water supplies is to collect good clean water to start with.

All water supply authorities will attempt to do this, but in practice the water in the main reservoirs is not good enough to simply pump out to peoples' homes. It is usually needs purifying and sanitizing by:

Flocculation of suspended solids

This achieved by adding Fe^{3+} ions which react with water forming highly insoluble iron(III) hydroxide, $\text{Fe}(\text{OH})_3$. The fine particles of $\text{Fe}(\text{OH})_3$ tend to join together and to adsorb particles of other fine suspended materials. This joining together is called "flocculation" and results in the suspended solids being in larger particles which either settle out, or can be filtered out, more quickly and efficiently.

Filtration

Many water supplies are filtered through beds of sand and carbon granules. This traps most of the flocculated solids, and the carbon tends to adsorb any organic chemical which can cause unpleasant odours and tastes.

Chlorination

After flocculation and filtration, the water is usually quite clean and clear, but may still carry small numbers of dangerous microbes.

To kill these, the usual practice is to add chlorine (Cl_2) to a concentration of about 2 ppm, which is sufficient to sanitize it. Lower levels might not kill all the microbes, and higher levels have a noticeable "chlorine taste".

Effectiveness of Treatments

Our water supply systems deal in millions of litres of water per day and there is always a compromise between meeting the needs of the community, and meeting quality and safety standards, and keeping the cost to a minimum.

Generally, the processes of filtration and sanitation seem to work effectively. In NSW, the number of health problems resulting from sub-standard water is zero in most years. Compared to the amount of illness and death occurring in parts of Africa where people are forced to use untreated water, we would have to conclude that our systems are very effective.

However, they are not infallible. In 1998 there was an outbreak of disease in the Sydney area, caused by a pathogen which survived the treatment processes. The actual number of cases was very low, but the public alarm (and media panic) was such to convince the authorities to do a better job.

There are ways to improve water treatment, at a cost.

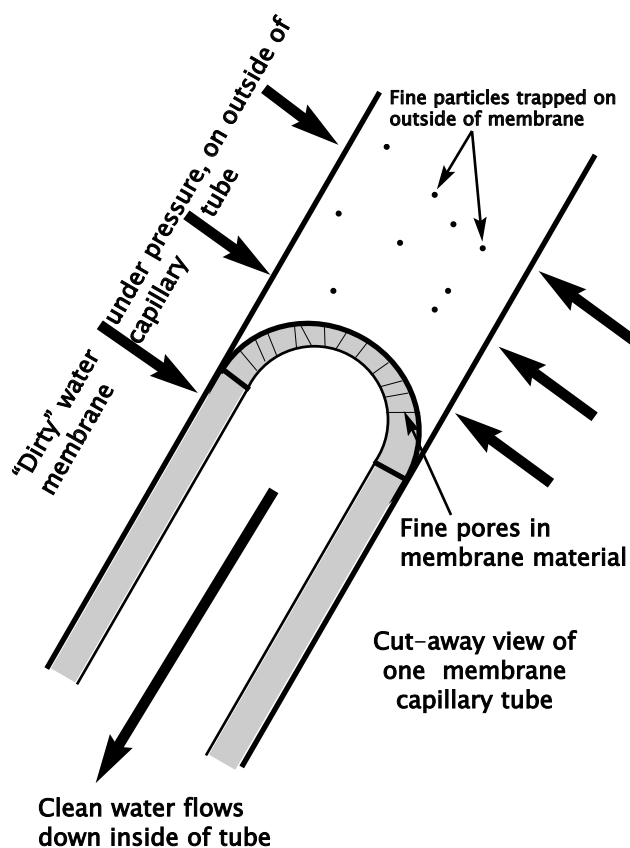
Microscopic Membrane Filters

Using plastics such as polypropylene, it is possible to make filters with extremely small pores in the material, as small as about 0.1 μm . ($1 \mu\text{m} = 1/1000 \text{ mm}$)

This is so fine that virtually all suspended particles (including living microbe cells and many viruses) can be filtered out of the water.

The usual system is to make the filter membranes into very fine, hollow "capillary tubes" (only 0.2 mm diameter). Although each is tiny, a bundle of thousands of them has a large surface area, and the strength of the polymer means that the water can be filtered under high pressure to speed up the throughput.

Generally, the "dirty" water is forced through the material from the outside, and a flow of clean water collected from the inside of the capillary tubes.



Membrane filters are very expensive compared to the existing sand filters, but very effective. In Singapore, a country with very limited water supplies, treated sewerage water is being filtered by microscopic membrane filters so effectively that it can be returned to the general water supply for re-use. In Australia, membrane filters are used mainly for filtering high quality bottled mineral waters.

Worksheet 5

Fill in the Blank Spaces

To monitor and ensure the quality of water supplies, a number of measurements and tests are useful:

- Turbidity is a measure of a)..... This is related to the presence of b)..... solids in the water. This is often measured by pouring water into a tall tube and observing c).....

- TDS stands for d)..... It can be measured by evaporating a sample and e)..... Electronic probes which measure f)..... can also be used for quick and accurate readings.

- “Hardness” is caused by dissolved g)..... and ions. Hard water causes h)..... in water pipes and prevents soap from i)..... This can be used as a qualitative test. Hardness can be assessed by the amount of j)..... formed when some soap and water samples are shaken.

- Acidity can be measured by k)..... or Unpolluted water should have a pH about l)..... Polluted water may have values m)..... or more pH units above or below this.

- BOD stands for n)..... This measures the change in o)..... when a sample is stored for 5 days. A large change indicates that p)....., and this means the water probably contains q).....

**WHEN COMPLETED, WORKSHEETS
BECOME SECTION SUMMARIES**

A number of factors influence which ions, and what concentrations, are dissolved in water.

- The Pathway. If water flows across natural bushland it will r)..... If it flows underground, it may dissolve s)..... and reach higher t)..... readings.

- The type of u)..... and the water flows over or through.

- The v)..... of the water. If water is more w)..... it will generally dissolve much more material.

- Human activities. If water flows through farmland it may dissolve a lot of x)..... and ions from y)..... Water seeping through a garbage dump could dissolve z)..... metals, such as aa)..... and

A method suitable to detect and measure even small quantities of heavy metals is AAS which stands for ab).....

“ac).....” refers to what happens to waterways if too much phosphate and nitrate get into them. These ions acts a ad)..... causing plants and algae to ae)..... and clog waterways. Then, when masses of plants die, the rotting process causes af).....

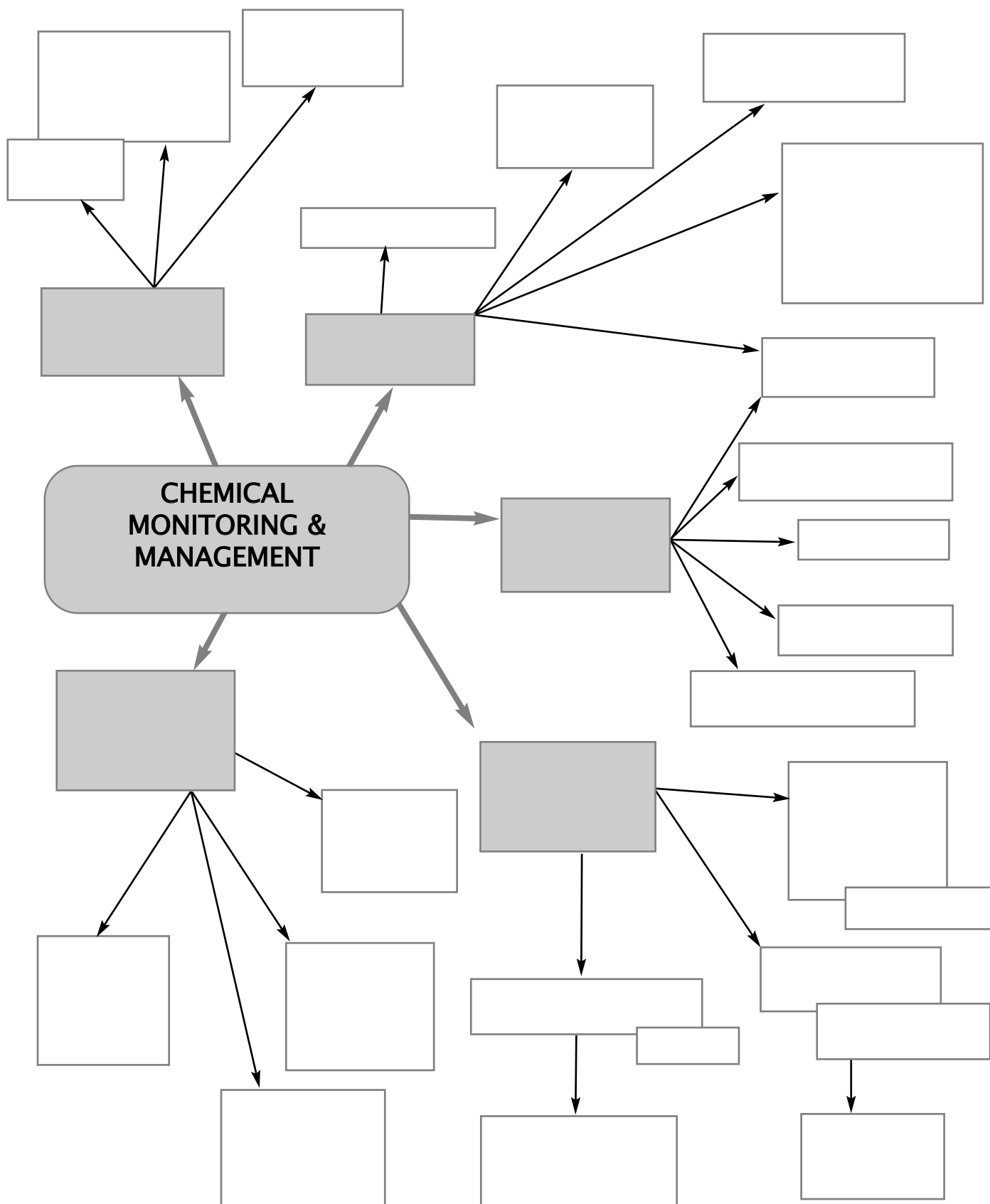
Generally, every water supply system treats the water to purify and ag)..... it. The first step is often to “ah).....” suspended solids. This means to make them “clump together” into larger particles. These are then removed by ai)..... the water through beds of aj)..... and Any remaining microbes are killed by treating the water with ak).....

An alternative treatment is to al)..... the water through Microscopic am)..... which can remove suspended solids and virtually all microbes.

CONCEPT DIAGRAM (“Mind Map”) OF TOPIC

Some students find that memorizing the **OUTLINE** of a topic helps them learn and remember the concepts and important facts.

Practise on this blank version.



Practice Questions

These are not intended to be "HSC style" questions, but to challenge your basic knowledge and understanding of the topic, and remind you of what you NEED to know at the K.I.S.S. Principle level.

When you have confidently mastered this level, it is strongly recommended you work on questions from past exam papers.

Part A Multiple Choice

1.

The need to monitor a chemical process is because even slight changes in conditions could alter:

- A. the pathway and products of the reaction.
- B. the rate of reaction and energy change.
- C. the equilibrium position and yield.
- D. all of the above.

2.

The industrial production of ammonia involves the reaction:



Increasing the temperature would be expected to:

- A. increase the yield and speed up the reaction.
- B. decrease the yield and speed up the reaction.
- C. increase the yield and slow down the reaction.
- D. decrease the yield and slow down the reaction.

3.

Samples of a solution known to contain one ionic compound were tested as follows:

added	Result
Cl^-	no reaction
SO_4^{2-}	no reaction
OH^-	blue precipitate
acid	no reaction
Ba^{2+}	white precipitate

The solution contains the compound

- A. barium hydroxide
- B. iron(II) sulfate
- C. copper(II) sulfate
- D. lead(II) chloride

4.

A flame test on a sample containing barium ions would be expected to flare:

- A. brick red
- B. lime-green
- C. yellow
- D. blue

5.

The analytical technique known as AAS would be suitable for measuring:

- A. trace amounts of arsenic in the hair of a murder victim.
- B. drug residues in the saliva of a sports person.
- C. the yield of ammonia in an industrial plant.
- D. the mass of lead in a bullet from a crime scene.

6.

The 4 most abundant gases in normal dry air are:

- A. nitrogen, oxygen, argon & carbon dioxide.
- B. oxygen, carbon dioxide, nitrogen & ozone.
- C. nitrogen, helium, oxygen & ozone.
- D. carbon dioxide, oxygen, argon & sulfur dioxide.

7.

At ground level, ozone is a pollutant gas associated with:

- A. incomplete combustion of fuels.
- B. smelting of metal ores.
- C. photochemical smog.
- D. emissions from chemical industries.

8.

Oxygen and ozone are examples of:

- A. isotopes.
- B. different elements.
- C. isomers
- D. allotropes.

9.

Which of the following chemical species is likely to form by coordinate covalent bonding?

- A. polyethylene
- B. potassium sulfide
- C. ammonium ion
- D. carbon dioxide

10.

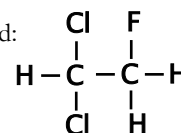
Which list places the 3 chemical species in increasing order of chemical reactivity?

- A. O_2 , O_3 , O^\bullet
- B. O^\bullet , O_2 , O_3
- C. O_3 , O^\bullet , O_2
- D. O_3 , O_2 , O^\bullet

11.

The compound shown would be called:

- A. 1,1-chloro-2-fluoroethane
- B. 1-fluoro-2,2-chloroethane
- C. 1,1-dichloro-2-fluoroethane
- D. 1-fluoro-2,2-dichloroethane



12.

CFC's are thought to cause ozone destruction in the Stratosphere because, when struck by U.V. rays, the CFC molecule:

- A. absorbs the U.V. so it does not penetrate to the ground.
- B. breaks apart, releasing a chlorine free-radical.
- C. attaches to an ozone molecule and immobilizes it.
- D. converts to different isomer.

13.

Water that is suitable for human consumption should have:

- A. very low BOD and turbidity.
- B. high dissolved oxygen and high BOD.
- C. low pH and high dissolved oxygen.
- D. high turbidity and high pH.

14.

A simple test for water “hardness” is to:

- A. taste it.
- B. add silver ions, and look for a precipitate.
- C. measure the pH.
- D. see if soap will lather in it.

15.

The addition of chlorine to water supplies is to:

- A. prevent tooth decay.
- B. flocculate suspended particles.
- C. test for the presence of silver ions.
- D. sanitize the water.

Longer Response Questions

Mark values shown are suggestions only, and are to give you an idea of how detailed an answer is appropriate.

16. (4 marks)

With reference to a specific job as a Chemical Scientist, outline 3 reasons for collaboration between scientists.

17. (7 marks)

In the Haber process for the industrial production of ammonia:

a) explain why hydrogen and nitrogen gases are mixed in a ratio of exactly 3:1. Include an equation in the explanation.

b) explain why the reactants are combined under a high pressure of about 300 atmospheres.

c) name the catalyst employed, and explain how it contributes to the process.

d) explain why the reaction temperature (about 400°C) is considered a “compromise”.

18. (5 marks)

In a qualitative analysis scheme for the cations Ba^{2+} , Ca^{2+} , Pb^{2+} , Cu^{2+} , Fe^{2+} and Fe^{3+} , and for the anions Cl^- , SO_4^{2-} , CO_3^{2-} and PO_4^{3-} , the following results were obtained for an ionic solution:

Added	Result
i) sulfate ion	no reaction
ii) hydroxide ion	green precipitate, turned brown
iii) barium ion	no reaction
iv) silver ion	white precipitate, darkened.

a) What is meant by a “qualitative” test?

b) For each test i)-iv) described above, state what this shows as either a positive, or negative, conclusion.

19. (7 marks)

In a gravimetric analysis of the purity of an ammonium sulfate fertilizer, a 5.47g sample was dissolved in dilute hydrochloric acid and filtered to remove insoluble solids. An excess of barium chloride solution was added, and the precipitate collected by filtration. The dried residue had a mass of 9.15g

- a) Write a balanced equation for the precipitation reaction.
- b) Calculate the % by mass of ammonium sulfate in the fertilizer.
- c) Describe one of the difficulties this analysis may present, and suggest how to overcome it.

20. (4 marks)

A Scientist was overheard to say:

“Ozone... good up there, bad down here”.

Explain in more detail what was meant by this comment.

21. (5 marks)

- a) Give a definition for “Coordinate Covalent Bond”.
- b) Using Lewis Formulas, explain the formation of an ozone molecule.
- c) Contrast the chemical reactivity and stability of the O_2 and O_3 molecules, and account for these differences.

22. (marks)

a) Outline 2 different methods used to monitor ozone concentrations in the upper atmosphere.

b) Give 2 significant findings that have come from ozone measurements taken over the past 30 years.

c) Discuss briefly 2 potential consequences that could arise from a continuation of the trends mentioned in part (b).

23. (8 marks)

Draw structural formulas for, and give systematic names of, four different isomers of dichloropropane.

24. (marks)

a) Write a series of equations (including a net equation) to show how ozone is destroyed by a chlorine free-radical.

b) Explain how the Cl^\bullet acts as a catalyst in this process.

25. (8 marks)

a) Describe in outline, how a BOD water test is carried out.

b) State the expected results you might obtain on a

i) sample of pure, healthy drinking water.

ii) water from a lake suffering “eutrophication”.

c) Explain what is meant by “eutrophication”, including mention of the usual chemical cause and its source(s).

26. (4 marks)

Our water supplies may have certain chemical substances added to them. Explain the reason(s) for adding:

- a) iron(III) chloride.
- b) chlorine.