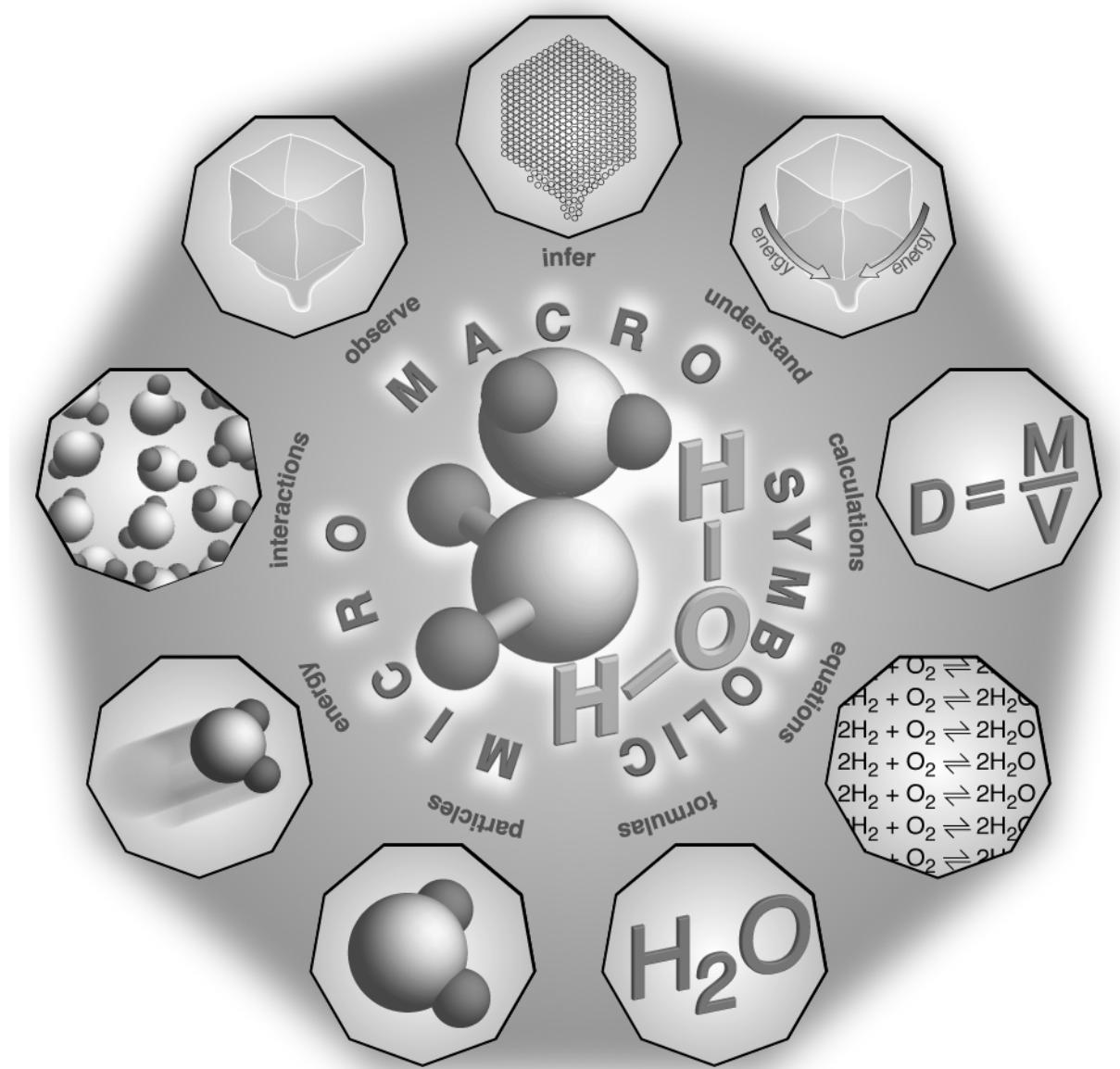




Chemical monitoring and management



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understand



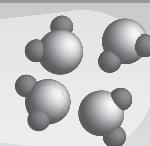
SYMBOLIC

H_2O formulas
equations
calculations



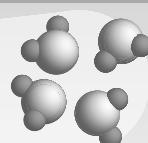
MICRO

particles
energy
interactions



Contents

Module overview	iii
Outcomes	iv
Indicative time.....	v
Resources.....	v
Icons	viii
Glossary.....	ix
Part 1: Monitoring and managing water quality	1-48
Part 2: Chemists at work	1-28
Part 3: Haber-Bosch process	1-26
Part 4: Chemical analysis.....	1-26
Part 5: CFCs and ozone	1-34
Part 6: Key ideas, key words and outcomes	1-22
Student evaluation of module	

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Module overview

The extracts below are from the *Chemistry Stage 6 Syllabus* © Board of Studies NSW, originally issued 1999. The most up-to-date version is to be found at http://www.boardofstudies.nsw.edu.au/syllabus99/syllabus2000_list.html

'The state of our environment is an important issue for society. Pollution of air, land and water in urban, rural and wilderness areas is a phenomenon that affects the health and survival of all organisms, including humans. An understanding of the chemical processes involved in interactions in the full range of global environments, including atmosphere and hydrosphere, is indispensable to an understanding of how environments behave and change. It is also vital in understanding how technologies, which in part are the result of chemical research, have affected environments. This module encourages discussion of how chemists can assist in reversing or minimising the environmental problems caused by technology and the human demand for products and services.'

The average human can survive about four minutes without air, four days without water and four weeks without food, a product of the land. The air of the atmosphere, the fresh water of the hydrosphere and the very thin soil layer on the surface of the lithosphere underpin the existence of human life on this planet. As humans have developed technologies to change their environment some of these changes have started to impact beyond local environments to the global environment. At the same time the increased chemical knowledge, understanding and skills that have flowed from these technologies can help chemists reverse or minimise environmental problems. Chemical problems require chemical solutions.

'Some modern technologies can facilitate the gathering of information about the occurrence of chemicals – both those occurring in natural environments and those that are released as a result of human technological activity. Such technologies include systems that have been developed to quantify and compare amounts of substances, including the mole concept and molarity.'

Quantitative chemical analysis now enables humans to establish baselines for natural environments and better measure and assess changes produced by human impact.

Outcomes

The main course outcomes to which this *Chemical monitoring and management* module contributes are:

A student:

- H2 analyses the ways in which models, theories and laws in chemistry have been tested and validated
- H3 assesses the impact of particular advances in chemistry on the development of technologies
- H6 explains reactions between elements and compounds in terms of atomic structures and periodicity
- H7 describes the chemical basis of energy transformations in chemical reactions
- H8 assesses the range of factors which influence the type and rate of chemical reactions
- H9 describes and predicts reactions involving carbon compounds
- H10 analyses stoichiometric relationships
- H11 justifies the appropriateness of a particular investigation plan
- H12 evaluates ways in which accuracy and reliability could be improved in investigations
- H13 uses terminology and reporting styles appropriately and successfully to communicate information and understanding
- H14 assesses the validity of conclusions from gathered data and information
- H15 explains why an investigation is best undertaken individually or by a team
- H16 demonstrates and justifies positive values about and attitude towards both the living and non-living components of the environment, ethical behaviour and a desire for critical evaluation of the consequences of the applications of science.

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Indicative time

This module is designed to take a minimum of thirty hours. There are a considerable number of practical activities in three of the six parts. Organising materials and equipment for carrying out all these activities could take additional time but in doing so you will better understand the type of work chemists do.

Resources

Materials and equipment you need to carry out activities are listed below. Access to a computer and the world wide web are important for the study of modern chemistry. An important skill to develop in chemistry is the planning ahead and thinking things through before carrying out the action. Make sure the resources you need are available when you start an activity. For details see the activity in the appropriate part.

For Part 1 you will require:

- potassium permanganate KMnO_4 crystals
- a teaspoon and a dropper
- two containers of at least 100 mL volume
- three small clean transparent containers such as test tubes, measuring cylinders, specimen tubes, that can hold at least 10 mL
- measuring cylinder or medicine measure for measuring 5 mL water.

Equipment to carry out at least two different quantitative tests on water samples from two different sources. Choose at least two of the following:

- pH: pH meter/pH indicator paper/pH indicator solution
- turbidity: two long thin transparent containers of uniform bore with a flat bottom such as long glass specimen tubes
- insoluble solids: sensitive weighing balance, filter paper, volume measure, filter
- total dissolved solids: EITHER sensitive weighing balance, filter paper, volume measure, filter, container which can be heated, heater OR conductivity meter
- chemical hardness: EITHER sensitive weighing balance, filter paper, volume measure, filter, Na_2CO_3 OR sensitive weighing balance, volume measure, 0.100 g of CaCO_3 , vinegar, soap solution, titration equipment

- dissolved oxygen: EITHER alkaline Mn(II) solution, acidified iodide solution, standardised sodium thiosulfate solution, starch solution and titration equipment OR dissolved oxygen probe and meter or datalogger.

For Part 2 you will require:

- access to a petrol engine car built since 1985.

For Part 3 you will require:

- small container such as a matchbox or for takeaway food
- small lollies/seeds to represent hydrogen such as cachous (silver balls)/hundreds and thousands or mustard seeds/peppercorns
- larger lollies/seeds to represent nitrogen such as Jila® mints or frozen peas
- a sticky substance to represent the catalyst surface such as jam/honey/vegemite®/peanut butter/mustard.

For Part 4 you will require:

- a laundry detergent with a stated level of phosphate
- 3 beakers or containers (at least 150 mL, 300 mL, 500 mL)
- filter paper and funnel or coffee filter paper
- epsom salt $MgSO_4 \cdot 7H_2O$ from a supermarket or pharmacy
- ammonia solution from a supermarket or hardware (at least 2.5% ammonia)
- a long handled spoon or stirrer
- a means of drying wet precipitate such as paper towels and an electric hotplate
- a means of weighing to at least the nearest gram
- a means of measuring about 50 mL volume of liquid
- titration equipment (burette, pipette, conical flask or small syringe, large syringe, medicine measure).

Quantities listed below are for burette, pipette and conical flask; if you use syringes and a medicine measure use one-tenth the quantities listed but you will need to be able to weigh the ammonium sulfate to 0.01 g.

- a means of weighing ammonium sulfate to at least 0.1 g
- 1.0 g ammonium sulfate $(NH_4)_2SO_4$
- heat resistant container such as a beaker of at least 300 mL capacity (to hold ammonium sulfate, NaOH solution and acid solution)

- 200 mL of 0.1 M NaOH solution such as used in Part 4 of the previous module *The acidic environment*
 - acid solution of known concentration such as the diluted vinegar used in Part 4 of the previous module *The acidic environment*
 - phenolphthalein or fresh red cabbage solution indicator
 - means of heating the container such as an electric hotplate
 - about one hour of time, spread over five days, to complete this activity as the precipitate of BaSO₄ needs to be left overnight to separate.
 - 1.0 g ammonium sulfate (NH₄)₂SO₄
 - a means of weighing to at least 0.1 g
 - 10 mL of a 1.0 M barium salt solution (about 2.5 g of barium acetate or barium chloride made up to 10 mL)
 - 10 mL measuring cylinder or a long specimen tube that could hold at least 12 mL
 - dropper (pasteur pipette and rubber teat works well) long enough to reach almost to the bottom of the measuring cylinder/specimen tube
 - filter papers or coffee filter paper from a supermarket
 - means of heating filter paper covered with BaSO₄ precipitate such as an electric hotplate.
 - a small container of orange juice
 - standardised NaOH solution about 0.1 M
 - phenolphthalein indicator
 - titration equipment (burette, measuring cylinder*, conical flask or small syringe, large syringe, medicine measure)
- * a pipette is unsuitable here as pulp in the orange juice blocks the jet

For Parts 4 and 5 you will require:

- computer access to the www

Icons

The following icons are used within this module. The meaning of each icon is written beside it.



The hand icon means there is an activity for you to do.
It may be an experiment or you may make something.



You need to use a computer for this activity.



There is a safety issue that you need to consider.



There are suggested answers for the following questions
at the end of the part.



There is an exercise at the end of the part for you to
complete.

Glossary

The following words, listed here with their meanings, are found in the learning material in this module. They appear bolded the first time they occur in the learning material.

AAS	atomic absorption spectroscopy; a technique able to measure the amount of an element present in ppm or ppb
absorbance	amount of light absorbed by a substance; measured values typically range from 0 (100% transmission of light) to 1 (90% transmission of light)
account for	state the reasons for
allotropes	different structural forms of the same element such as diamond and graphite forms of carbon
analyse	identify components and the relationship between them; draw out and relate implications
aspiration	drawing up of a fluid
assess	make a judgement of value, quality, outcomes, results or size
back titration	titration method used for a slow reaction or reaction involving heating or a solid – a known volume of excess reactant is added, the amount of excess reactant is determined by titration
backwashing	reversing the flow of water in a filter to clean the filter and discard the washings
bioaccumulation	increasing concentration of a chemical in the bodies of organisms along a food chain
BOD	biochemical oxygen demand
calibration curve	line drawn to compare measurements for different concentrations of a substance
catchment	area from which something comes; a water catchment is land bounded by hills or mountains from which surface or ground water flows
chloramination	addition to water of chlorine followed by ammonia for longer lasting destruction of microbes
CFC	chlorofluorocarbon

coagulation	coming together of colloidal particles
collaboration	working together effectively
colloidal solution	solution containing particles between 10^{-9} and 10^{-6} metres
combustion	burning; reaction with oxygen releasing heat energy
compare	show how things are similar or different (by words/labelled diagrams/table.)
conservation	use, management and protection of resources so that they are not degraded, depleted or wasted and are available on a sustainable basis for present and future generations
coordinate covalent bond	covalent bond where the shared pair of electrons comes from only one of the atoms joined
cryptosporidium	diarrhoea causing organism
decant	pour liquid off the top of a container
describe	provide characteristics and features
detergent	surface active agent
discuss	identify issues and provide points for and/or against
DO	dissolved oxygen
environmental indicators	physical, chemical or biological factors that are monitored and used to measure change
EPA	Environmental Protection Agency
eutrophication	increase in nutrient content of a body of water resulting in excessive growth of organisms, decay and depletion of oxygen concentration
evaluate	make a judgement based on criteria; determine the value of
explain	give cause and effect; make the relationships between things evident; give reasons
fertiliser	chemical added to soil to improve plant growth
flame test	test for an element using the colour emitted by a flame by that element or a compound containing the element.
flocculation	precipitation of particles formed from colloids

fluorescent	material which emits coloured light almost immediately after absorption of UV
free radical	atom or molecule with unpaired electron(s)
giardia	diarrhea causing organism
ground state	all electrons in an atom are in their lowest possible energy level
habitat	place where an animal or plant normally lives
haloalkane	saturated hydrocarbon containing at least one halogen atom per molecule
heavy metal	metal with a density above 5 g cm^{-3}
heterogeneous catalysis	catalyst and reactants are in different phases
hollow cathode lamp	lamp with a hollow cathode made of a solid element used to emit wavelengths characteristic of that element; used in AAS
homogeneous catalysis	catalyst and reactants are in the same phase
identify	recognise and name
isomers	different structural forms of the same molecular formula
justify	support an argument or conclusion with reasons
lather	foam of soap, air and water
latitude	angular distance from the equator (0°) to the poles (90°)
LC ₅₀	lethal concentration that kills 50% of the sample of one type of living thing
management	handling, direction and control of a situation
monitoring	checking, observing or recording a situation; testing program to assess potential changes
nitrogen fixation	changing of nitrogen in the atmosphere to nitrogen in compounds used by plants
N:P	nitrogen to phosphorus ratio by weight
outline	give the main features of
pharmacopeia	book listing chemical information about drugs
predict	suggest what might happen
pungent	sharp odour

qualitative	concerned with quality
quality	characteristic, property or purity
quality control	monitoring samples to manage quality of product
quantitative	concerned with quantity
refrigerant	liquid which circulates through the compressor and coils of a refrigerator
sanitise	make disease free
screen	filter for trapping visible particles
sewage	waste water
spectrometer	instrument for measuring different wavelengths of electromagnetic radiation
spectroscopist	person who uses a spectrometer
spectroscopy	study of spectra
stormwater	water that runs off buildings and the ground into gutters and drains and then to creeks, rivers, harbour or ocean
stratopause	layer of air of uniform temperature above the stratosphere
stratosphere	'upper atmosphere'; layer of atmosphere between 20 and 50 km altitude
suspension	particles of solid suspended in water
synthesis	building up a substance from simpler ones
TDS	total dissolved solids
temperature inversion	layer of warm air above cool air
toxin	poison produced by a living thing
trace element	element found in a living thing or soil in very small amounts that is important to living things
tropopause	layer of air of uniform temperature between the troposphere and stratosphere
troposphere	'lower atmosphere'; layer of atmosphere closest to ground
turbidity	opaqueness or cloudiness of water
UV	ultraviolet radiation

Chemistry

HSC Course

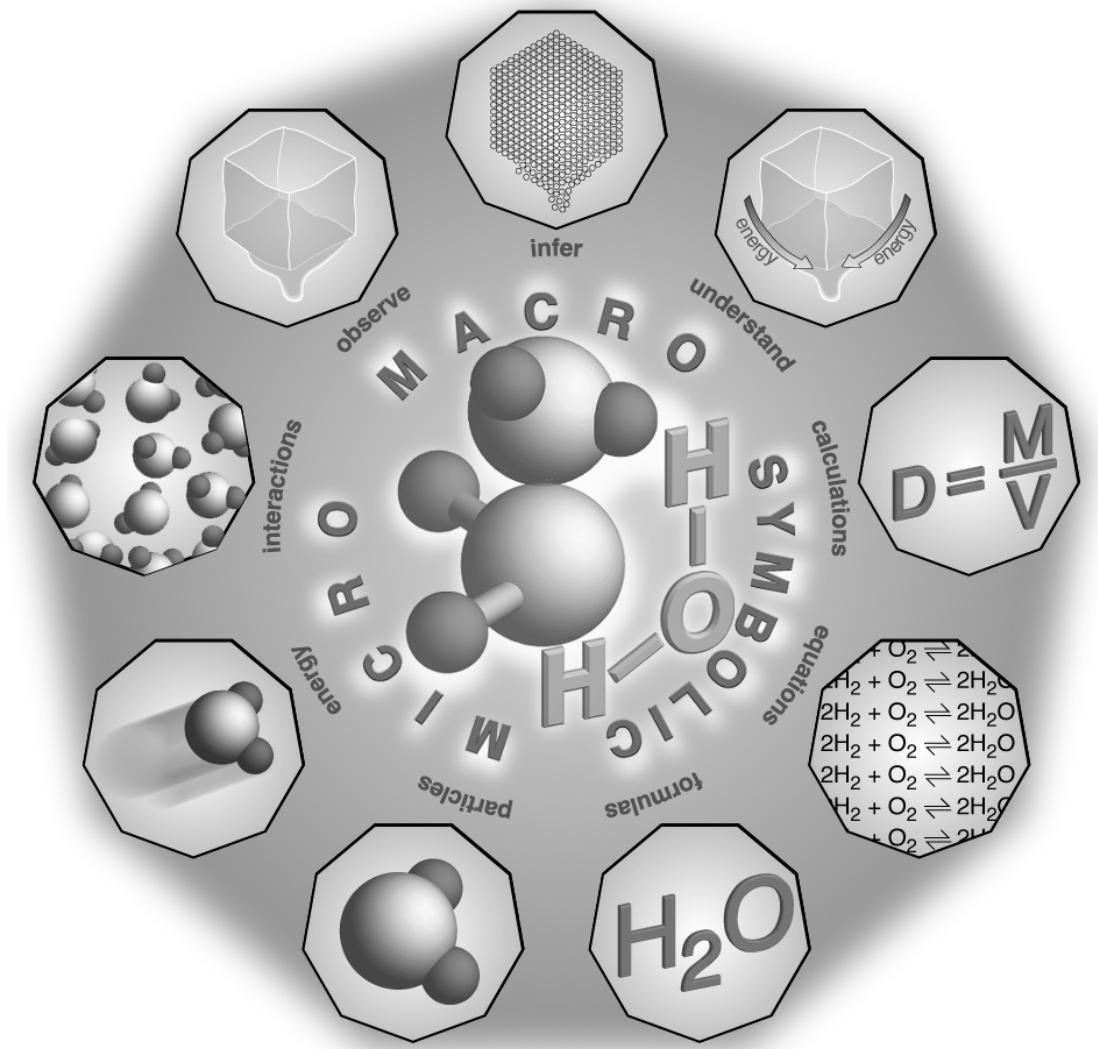
Stage 6

NEW SOUTH WALES
DEPARTMENT
OF EDUCATION
AND TRAINING



Chemical monitoring and management

Part 1: Monitoring and managing water quality



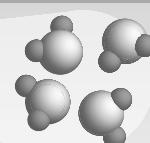
1	H Hydrogen	1.008
3	Li Lithium	6.94
11	Na Sodium	22.99
19	K Potassium	39.10
37	Rb Rubidium	85.47
55	Cs Cæsium	132.9
87	Fr Francium	[223.0]

1	H Hydrogen	1.008
3	Be Beryllium	9.01
11	Mg Magnesium	24.31
19	Ca Calcium	40.08
37	Sr Strontium	87.62
55	Ba Barium	137.3
87	Ra Radium	[226.0]

1	H Hydrogen	1.008
3	Be Beryllium	9.01
11	Mg Magnesium	24.31
19	Ca Calcium	40.08
37	Sr Strontium	87.62
55	Ba Barium	137.3
87	Ra Radium	[226.0]
19	Sc Scandium	44.96
39	Ti Titanium	47.87
41	V Vanadium	50.94
42	Cr Chromium	52.00
43	Mn Manganese	54.94
44	Fe Iron	55.85
45	Co Cobalt	58.93
46	Ni Nickel	58.69
47	Pd Palladium	106.4
48	Rh Rhodium	102.9
49	Ru Ruthenium	101.1
50	Tc Technetium	[98.91]
51	Mo Molybdenum	95.94
52	Nb Niobium	92.91
53	Zr Zirconium	91.22
54	Y Yttrium	88.91
55	La Lanthanides	57.71
56	Ce Lanthanides	72
57	Gd Lanthanides	73
58	Pr Lanthanides	74
59	Eu Lanthanides	75
60	Sm Lanthanides	76
61	Tb Lanthanides	77
62	Dy Lanthanides	78
63	Ho Lanthanides	79
64	Er Lanthanides	80
65	Tm Lanthanides	81
66	Yb Lanthanides	82
67	Lu Lanthanides	83
68	Y Lanthanides	84
69	Erbium	85
70	Ytterbium	86
71	Lu	87
72	Th Actinides	88
73	Rf Rutherfordium	89-103
74	Bh Bohrium	104
75	Db Dubnium	105
76	Hs Hassium	106
77	Mt Meitnerium	107
78	Uuu Ununtrium	108
79	Uun Ununnilium	109
80	Uub Ununnilium	110
81	Uup Ununnilium	111
82	Uuuq Ununnilium	112
83	Uuh Ununnilium	113
84	Uuh Ununnilium	114
85	Uuh Ununnilium	115
86	Uuo Ununoctium	116
87	Uuo Ununoctium	117
88	Uuo Ununoctium	118

57	La Lanthanum	138.9
89	Ac Actinium	[227.0]
90	Th Thorium	232.0
91	Pa Protactinium	231.0
92	U Uranium	238.0
93	Np Neptunium	[237.0]
94	Pu Plutonium	[239.1]
95	Cm Curium	[241.1]
96	Am Americium	[244.1]
97	Bk Berkelium	[249.1]
98	Cf Californium	[252.1]
99	Es Einsteinium	[257.1]
100	Fm Fermium	[258.1]
101	Md Mendelevium	[259.1]
102	No Nobelium	[259.1]
103	Lr Lawrencium	[262.1]

1	H Hydrogen	1.008
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42	Mn Manganese	52.00
43	Fe Iron	54.94
44	Co Cobalt	55.85
45	Ni Nickel	58.93
46	Pd Palladium	63.55
47	Rh Rhodium	65.39
48	Ru Ruthenium	69.72
49	Tc Technetium	72.61
50	Mo Molybdenum	74.92
51	Nb Niobium	76.90
52	Zr Zirconium	79.90
53	Y Yttrium	83.80
54	La Lanthanides	88.00
55	Ce Lanthanides	91.22
56	Gd Lanthanides	93.22
57	Pr Lanthanides	94.22
58	Eu Lanthanides	95.22
59	Sm Lanthanides	96.22
60	Tb Lanthanides	97.22
61	Dy Lanthanides	98.22
62	Ho Lanthanides	99.22
63	Er Lanthanides	100.22
64	Yb Lanthanides	101.22
65	Lu Lanthanides	102.22
66	Erbium	103.22
67	Ytterbium	104.22
68	Lu	105.22
69	Th Actinides	106.22
70	Yttrium	107.22
71	Lu	108.22
72	Th Actinides	109.22
73	Pa Protactinium	110.22
74	U Uranium	111.22
75	Np Neptunium	112.22
76	Pu Plutonium	113.22
77	Cm Curium	114.22
78	Bk Berkelium	115.22
79	Cf Californium	116.22
80	Es Einsteinium	117.22
81	Fm Fermium	118.22
82	Md Mendelevium	119.22
83	No Nobelium	120.22
84	Lr Lawrencium	121.22
85	Fr Francium	122.22
86	Rn Radium	123.22
87	Ra Radium	124.22
88	Ac Actinium	125.22
89	Th Thorium	126.22
90	Pa Protactinium	127.22
91	U Uranium	128.22
92	Np Neptunium	129.22
93	Pu Plutonium	130.22
94	Cm Curium	131.22
95	Bk Berkelium	132.22
96	Cf Californium	133.22
97	Es Einsteinium	134.22
98	Fm Fermium	135.22
99	Md Mendelevium	136.22
100	No Nobelium	137.22
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equations
calculations**MICRO**particles
energy
interactions

Contents

Introduction	3
What is monitoring?.....	5
What is management?	7
Water quality	8
Quantitative analysis of water samples	13
pH	13
Turbidity	13
Insoluble solids	14
Total dissolved solids (TDS)	15
Chemical hardness	17
Dissolved oxygen (DO)	19
Common ions	22
Eutrophication of waterways and the N:P ratio.....	26
Monitoring and managing N:P	27
Membrane filters.....	30
At the Sydney Olympics site.....	32
Heavy metal pollution.....	35
Water filtration plants.....	36

Appendix	39
Suggested answers	41
Exercises – Part 1.....	47

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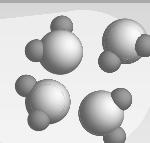
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Introduction

Much of the improvement in human life expectancy since the industrial revolution can be attributed to the provision of better quality drinking water. However major difficulties facing the world's increasing population are providing enough water for all and the impact of human activity on waterways. Chemical monitoring and management assists in providing safe water for human use and in protecting the habitats of other organisms.

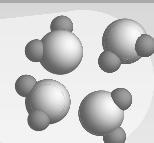
In Part 1 you will be given opportunities to learn to:

- identify and describe tests that can be used to determine the quality of water samples as:
 - concentrations of common ions
 - total dissolved solids (TDS)
 - hardness
 - turbidity
 - acidity
 - dissolved oxygen (DO) and biochemical oxygen demand (BOD)
 - nitrogen-to-phosphorus ratio (N:P)
- identify factors that affect the concentrations of a range of ions in solution in natural bodies of water such as rivers and oceans
- describe and assess techniques for accurate determination of masses of solids in water samples
- describe and assess the effectiveness of methods used to purify and sanitise mass water supplies
- describe the design and composition of microscopic membrane filters and explain how they purify contaminated water.

In Part 1 you will be given opportunities to:

- perform first-hand investigations to use qualitative and quantitative tests to analyse and compare the quality of water samples
- gather, process and present information on the range and chemistry of the tests used to:
 - identify heavy metal pollution of water
 - monitor possible eutrophication of waterways
- perform first-hand investigations to test for solids in water samples from the local environment
- gather, process and present information on the features of the local town water supply in terms of:
 - catchment area
 - possible sources of contamination in this catchment
 - chemical tests available to determine levels and types of contaminants
 - physical and chemical processes used to purify water
 - chemical additives in the water and the reasons for the presence of these additives.

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equations
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What is monitoring?

Monitoring is checking, observing or recording a situation.

Monitoring of water quality can be:

- **qualitative**, such as when human senses check that water is
 - colourless
 - clear (transparent and lacking turbidity)
 - odourless
 - good taste without any saltiness
- **quantitative**, such as when chemicals and/or equipment are used to measure the amount of:
 - turbidity (opaqueness, mostly due to suspended clay particles absorbing light)
 - total dissolved solids (TDS)
 - chemical hardness (hard water is hard to lather with soap)
 - acidity (pH)
 - dissolved oxygen (DO)
 - nitrogen
 - phosphorus
 - heavy metals such as Hg, Pb and Cd.



Qualitative analysis of your drinking water supply and another water sample.

Qualitative test	Human sense used	Drinking water	_____ water
colour			
clarity			
odour			
taste			don't taste !



- 1 Why is it okay to taste the drinking water but not the other water sample?

- 2 If one of your results for the _____ water was different from drinking water suggest a hypothesis.

Boil a sample of your drinking water supply and let it cool back to room temperature before repeating the qualitative tests.

Qualitative analysis of boiled drinking water.

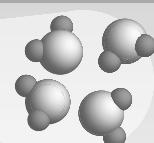
Qualitative test	Human sense used	Your observation
colour		
clarity		
odour		
taste		

- 3 If any of your results for the boiled drinking water were different from drinking water suggest a hypothesis.

Check your answers.

Qualitative monitoring of your water supply could reveal:

- stained clothes after washing (red/brown could be caused by Fe, black by Mn, green/blue by Cu)
- rotten egg gas odour (H_2S)
- metallic taste (Fe, Zn, Cu, Pb)
- salty taste (NaCl)
- bleach-like odour (chlorine)
- corrosion or pitting of metal (acid pH)
- deposits on the insides of kettles, electric jugs or irons (CaCO_3 deposited from hard water)
- darkening of tooth enamel (high F^- concentrations in some bore or artesian waters).

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What is management?

Management is the handling, direction and control of a situation.

How you obtain and spend money and how you prepare for your next chemistry assessment are examples of management.

Monitoring is a part of management. After you have monitored a situation you may need to make management decisions and carry out management actions. Looking at how much money is in your bank account is monitoring money. Management of money involves depositing and withdrawing from your account and making decisions on what to spend and save.

Monitoring water quality provides information helpful in the management of water supplies.

- 1 What is your next chemistry assessment task?



- 2 When is your next chemistry assessment task to be done or completed?

- 3 Where are the notes you should revise before doing this chemistry assessment task?

- 4 What equipment will you need to provide for your next chemistry assessment task?

- 5 Give an example of a monitoring you could carry out as part of managing your preparation for the next chemistry assessment task.

Compare your answers.

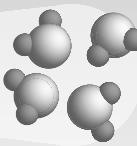
MACRO

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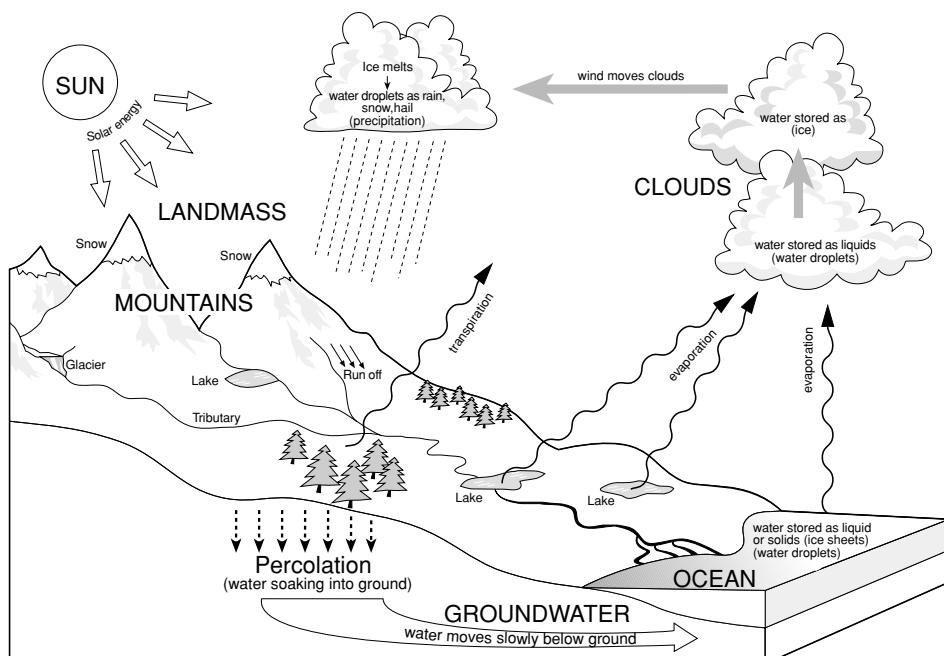
H_2O formulas
equations
calculations



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particles
energy
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Water quality



The water cycle.

Rainwater contains dissolved gases many of which make the water acidic. Rainwater falling over oceans or on land in coastal areas contains salt dissolved from sea spray.



List formulas of gases from air which can make water acidic.

Check your answers.

Surface water becomes more acidic as it dissolves organic acids and carbon dioxide produced by decaying plants. Salts are dissolved from the soil and the amount and type of salt dissolved can depend on pH of the water and the type of soil and surface rock. Common ions in surface water are Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and HCO_3^- . Al^{3+} is common after acid rain. Rivers can be polluted by disposal of waste water (sewage).

Ground water that has percolated through rock layers contains less oxygen and a greater variety and concentration of ions than surface water. Any iron ions are usually light green iron (II) and when this water reaches the surface oxidation by oxygen in air produces brown iron (III). $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$. Ground water can be contaminated by buried waste, industrial waste sites or underground layers such as those containing As.

Sea water is about 3.5% salt (35 000 ppm salt). The presence of so many ions in sea water lowers the ability of non-polar oxygen molecules to dissolve. Sea water usually contains a lower concentration of oxygen than fresh water.

Ion	Rain water	Surface water	Sea water
Na^+	2.0	6.0	10770
Cl^-	4.0	8.0	19500
Mg^{2+}	0.3	4.0	1300
SO_4^{2-}	2.0	12	1000
Ca^{2+}	0.6	15	400
K^+	0.3	2.0	400
HCO_3^-	0.1	60	30
F^-	0.0	0.0	1.0

Typical ion concentrations in ppm (w/w).



Use the data in the table and your general knowledge to decide whether the following statements are true (T) or false (F).

- 1 The rainwater contains no fluoride ions. _____
- 2 The rainwater could contain 0.04 ppm fluoride ions. _____
- 3 The sea water data must be wrong because the $\text{Na}^+:\text{Cl}^-$ in salt is 1:1

Check your answers.



Write the chemical name for each of the following substances beside their formulas.

Hg _____

Pb _____

Cd _____

Mn _____

H₂S _____

CaCO₃ _____

F⁻ _____

Check your answers.

Visualising a concentration of 1 ppm



What you will need:

- potassium permanganate KMnO₄ crystals
- a teaspoon and a dropper
- two containers of at least 100 mL volume
- three small clean transparent containers such as test tubes, measuring cylinders, specimen tubes, that can hold at least 10 mL
- measuring cylinder or medicine measure for measuring 5 mL water.



Note: Handle KMnO₄ solutions with care. The concentrations prepared here are not hazardous but KMnO₄ is the most intensively coloured common chemical known. If you spill it on clothes or skin and do not wash it off straight away it leaves harmless but unsightly brown stains.

What you will do:

- 1 Scoop potassium permanganate crystals into a teaspoon so that an area about the size of a five cent coin at the bottom of the spoon is covered with the crystals. You now have about 0.5 g of one of the most intensively coloured chemicals known, KMnO₄.
- 2 Add 50 mL of water to one of the larger containers.
- 3 Add the 0.5 g of crystals to the 50 mL (50 g) of water and stir for at least a minute so that all the crystals dissolve.
You have prepared a solution where the concentration of KMnO₄ is
 $0.5 \text{ g}/50 \text{ g} = 1/100 = 10\ 000/1\ 000\ 000 = 10\ 000 \text{ ppm}$.
- 4 Decant this solution into another container to make sure all the crystals dissolved.

If some crystals are undissolved pour the solution back onto the crystals and stir for at least another minute. Repeat this action until all the crystals have dissolved.

- 5 A drop of water is approximately $0.05 \text{ mL} = 0.05 \text{ g}$ of water. Add one drop of the 10 000 ppm solution to 5 mL of water in one of the small containers and shake well to prepare a 100 ppm solution. Line the two solutions up so you can compare their appearances.
- 6 Wash out the dropper three times with water. Fill it with the 100 ppm solution and empty it at least once to ensure any solution transferred is not diluted with water. Add one drop of the 100 ppm solution to 5 mL of water in another container and shake well to prepare a 1 ppm solution.
- 7 Pour 5 mL of the 10 000 ppm into the remaining small container. Record the appearances of the three solutions in the results table.



Results:

Complete the two tables below.

KMnO ₄ concentration (ppm)	Colour of solution
10 000	
100	
1	

KMnO ₄ concentration (ppm)	Weight of KMnO ₄ in each drop(g)
10 000	0.0005 = 500 micrograms
100	0.000005 = micrograms
1	= 0.05 micrograms

Questions:

- 1 Does the colour of a solution depend on the thickness of the solution you are looking at? Compare looking at the same solution from above and from the side.

- 2 Electronic balances that weigh in micrograms are very expensive. If you have a chemical that does not react with a solvent, such as KMnO₄ and water, you can still measure out microgram amounts of the chemical without using a microgram balance. How would you do this?

Check your answers.

Conclusion: It (is/is not) possible to prepare a 1 ppm solution of KMnO₄ in water and see the colour of the permanganate ions.

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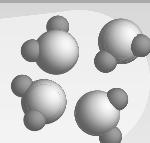
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Quantitative analysis of water samples



Carry out at least two different quantitative tests on samples from two different sources.

You are expected to identify and describe all of these tests so make sure you learn about all the tests and attempt all questions asked.

pH

Measure the pH using a pH meter, pH indicator paper or pH indicator solution.

Turbidity

To measure relative turbidity you will need two long thin transparent containers of uniform bore with a flat bottom such as long glass specimen tubes. Draw a black cross on a white tile or sheet of paper. Place the black cross under the bottom of a uniform bore container.

Looking from above, slowly pour your water sample into the tube until you can no longer see the black cross. Measure the depth of solution.

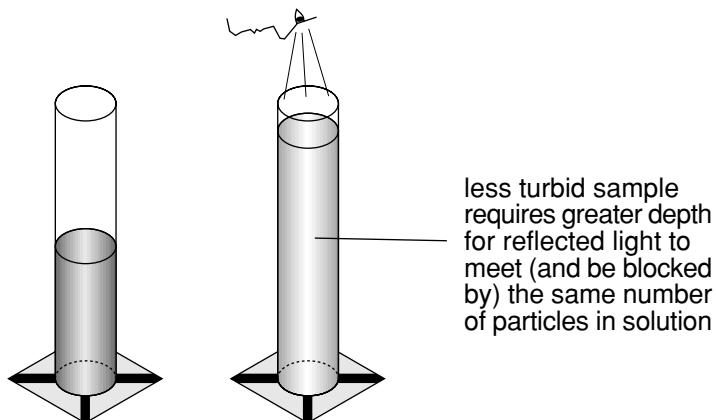
Using a different water sample repeat the procedure and once again measure the depth of solution required so the black cross cannot be seen.

If the tube is not high enough draw and use a fainter black cross.

Turbidity sample A:Turbidity sample B=depth sample B: depth sample A

If sample A requires 1/2 the depth of sample B it has 2 x the turbidity

If sample A requires 1/3 the depth of sample B it has 3 x the turbidity.



Insoluble solids

This method requires a sensitive weighing balance.

- 1 Weigh a filter paper.
- 2 Filter a known volume of water using the previously weighed filter paper.
- 3 Dry the filter paper and trapped insoluble solids and reweigh.
Repeat the drying and reweighing until a constant weight is obtained.

Calculate the concentration of insoluble solids in gL^{-1} using the following results.

Weight of filter paper 0.82 g

Volume of water filtered 500 mL

Measurement	Weight of dried filter paper + insoluble solid (g)
1	1.88
2	1.76
3	1.73
4	1.72
5	1.71
6	1.71



- 1 Concentration of insoluble solid in g/L =

- 2 Calculate the concentration of insoluble solid in mg/L = ppm.

Check your answers.

Total dissolved solids (TDS)

By evaporation

Filter out insoluble solids from the water sample.

Weigh a clean, dry container which can be heated, can be weighed accurately and which is large enough to hold all of the water sample.

Add a measured volume of the filtered water sample to the container.
Weigh the container and water sample.

Heat the container until it boils gently.

Remove the source of heat when practically all the water has evaporated.
Heat carefully so that 'spitting' (ejection of dry material from the container) does not occur.

Cool the container then weigh it to determine the amount of solid in the sample. Calculate the concentration in mg/L = ppm.



- 1 Why must a water sample be filtered before using this method to determine TDS?

- 2 Calculate the TDS in ppm using the data below:

Volume of filtered water 1000 mL

Weight of clean, dry container 250.76 g

Weight of container and filtered water 1250.28 g

Weight of container after evaporation 251.13 g

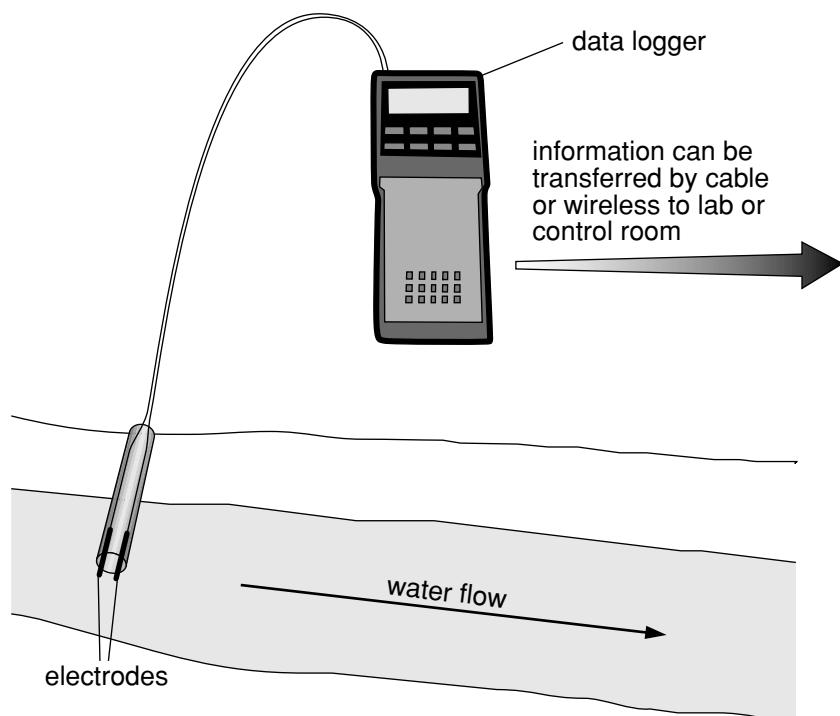
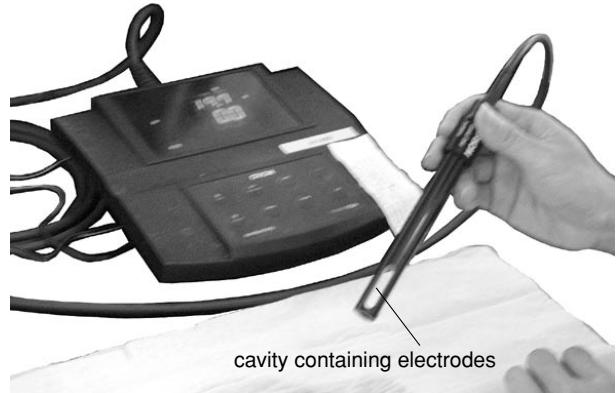
3 Is the ppm figure you calculated w/v, v/w, v/v or w/w? _____

Check your answers.

Using a conductivity meter

Most dissolved solid such as NaCl is ionic salt. The greater the concentration of dissolved salt the higher the electrical conductivity.

Electrical conductivity measurements can be made using a small meter like a 'stick' pH meter. In a river, dam or industrial process a conductivity meter connected to a datalogger can keep a continuous record of dissolved ionic solids.



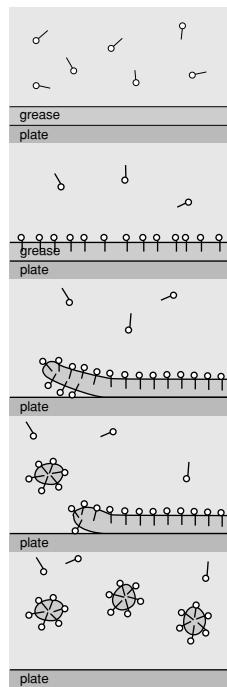
Chemical hardness

Chemical hardness is caused by ions such as Ca^{2+} and Mg^{2+} which form insoluble salts with soap ions. The insoluble calcium and magnesium soap scum floats on top of the water removing soap ions from solution. The water is 'hard' to **lather** (produce a foam of soap bubbles).

Soaps are water soluble sodium or potassium salts of alkanoic acids with typically 12 to 18 carbon atoms. A soap ion can be represented as a line with a circle on the end. The line represents the hydrophobic carbon chain while the circle represents the hydrophilic $-\text{COO}^-$ polar group.



The five diagrams following show how a soap solution can remove grease from a plate. Match each of the five diagram labels to the appropriate diagram.



With some agitation small globules of oil are lifted away from the plate.

Soap solution is added to the greasy plate.

Soap ions arrange themselves with the hydrophobic carbon chain in grease and the hydrophilic polar group in water.

Soap ions surround oil globules preventing them from joining together and keeping them suspended in the soapy water which turns darker.

Soap ions help separate grease from the plate.

Check your answers.

Gravimetric method precipitating carbonates

The Ca^{2+} and Mg^{2+} ions that cause hardness can be precipitated out of solution by the addition of a soluble carbonate such as Na_2CO_3 (washing soda).

The precipitate from a known volume of water can be filtered off, dried and weighed. Most hardness is due to Ca^{2+} so the precipitate is assumed to be CaCO_3 . $\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CaCO}_3(\text{s})$



4.00 L of hard water precipitated carbonate after addition of excess Na_2CO_3 . The dried precipitate weighed 3.48 g. Assuming all precipitation was due to calcium ions calculate the concentration of calcium ions in mol L^{-1} and ppm.

Complete these calculations.

Formula mass of CaCO_3 = _____ g/mole

3.48 g = 3.48/ _____ = _____ mol CaCO_3

each CaCO_3 contains one calcium ion thus concentration of Ca^{2+}

= _____ mol/ _____ L = _____ mol L^{-1}

_____ mol Ca^{2+} = _____ \times 40.08 g = _____ g

1.00 L of water = 1 000 g

_____ mol L^{-1} Ca^{2+} =

= _____ ppm

Check your answers.

Soap titration method

- 1 Prepare a standard solution containing calcium ions in distilled water eg. 100ppm CaCO_3 can be made by dissolving 0.100 g of CaCO_3 in a small amount of vinegar and making up to a volume of 1.00 L.
- 2 Prepare a soap solution by completely dissolving small pieces of soap in distilled water
- 3 Transfer 25.0 mL of the standard solution to a conical flask and titrate with vigorous shaking against a soap solution from a burette or syringe. The end point is reached when the vigorous shaking produces lather.
- 4 Transfer 25.0 mL of the hard water sample to a conical flask and titrate with vigorous shaking against the same soap solution from a burette or syringe. The end point is reached when the vigorous shaking produces lather.



25 mL of a standard 100 ppm CaCO_3 solution required 5.00 mL of soap solution before it lathered. 25 mL of a hard water solution required 15.0 mL of the same soap solution before it lathered.

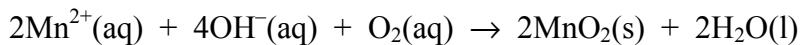
Mentally calculate the hardness of the hard water solution in ppm CaCO_3 . (Don't reach for your calculator! You should be able to do this calculation mentally. Think about what happened and try and work out the answer without using a calculator or putting pen to paper.)

Check your answers.

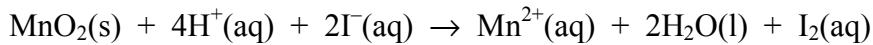
Dissolved oxygen (DO)

The Winkler method is a way of fixing the amount of dissolved oxygen in a sample and determining the DO by titration at a later time.

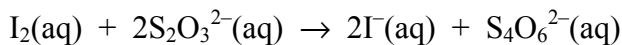
Manganese(II) ions and hydroxide ions are added to the water sample. The amount of insoluble brown manganese(IV) oxide produced depends on the amount of DO.



Acidified iodide solution reacts with the MnO_2 producing a yellow iodine solution.



The iodine released is titrated against a standard sodium thiosulfate solution from a burette using starch indicator. The starch indicator forms a blue colour with iodine; the blue colour disappears at the endpoint.



From the above equations you can see that each dissolved O_2 molecule gives 2MnO_2 which gives 2I_2 which react with $4\text{S}_2\text{O}_3^{2-}$.

Thus for each mole of thiosulfate used at the end in the titration there was 1/4 mole of dissolved oxygen in the original sample.

When water samples are collected from different locations identical containers, identical sealing systems and the same collection procedure should be used. If dissolved oxygen is to be measured it is important:

- the containers are completely filled with water so there is no air space
- the containers are kept out of light so algae present cannot add to the oxygen level by photosynthesis.



A 500 mL sample of river water was analysed for DO using the Winkler method. 5.40 mL of 0.0500 molL⁻¹ thiosulfate was needed for the titration.

Complete the calculations for the DO level.

$$\text{mol thiosulfate} = 5.40 \times 10^{-3} \times 0.0500 = \underline{\hspace{2cm}}$$

$$\text{mol oxygen} = 1/4 \times \underline{\hspace{2cm}} = \underline{\hspace{2cm}}$$

$$\begin{aligned}\text{Molar concentration of oxygen} &= \underline{\hspace{2cm}} \text{ mol / 0.500 L} \\ &= \underline{\hspace{2cm}} \text{ molL}^{-1}\end{aligned}$$

$$\text{mol oxygen in each litre} = \underline{\hspace{2cm}}$$

$$\text{mass of oxygen in each litre} = \underline{\hspace{2cm}} \times 32.0 \text{ g} = \underline{\hspace{2cm}} \text{ g}$$

$$\begin{aligned}\text{ppm of oxygen} &= \text{mass of oxygen in one litre / mass of one litre of water} \\ &= \underline{\hspace{2cm}} \text{ g} \quad / \quad 1\,000 \text{ g} \\ &= \underline{\hspace{2cm}} \text{ ppm}\end{aligned}$$

Below 5 ppm DO animal populations such as fish do not normally survive.

Another important indicator of water quality is biochemical oxygen demand (BOD). Two water samples are taken. One sample is measured for DO while the other is stored in a dark place at a constant temperature (about 20°C) for five days before its DO is measured. The five day sample will have a lower DO level because carbon compounds in the water will react with oxygen, aided by microorganisms, over the five days.

$$\text{BOD}_5 = \text{DO}_{\text{initially}} - \text{DO}_{\text{after five days}}$$

A very healthy body of water has a BOD of 1 or 2 ppm.

- 1 Why must the second sample be stored in the dark to obtain a valid BOD?

- 2 Why is the water temperature measured when DO samples are collected?

Check your answers.

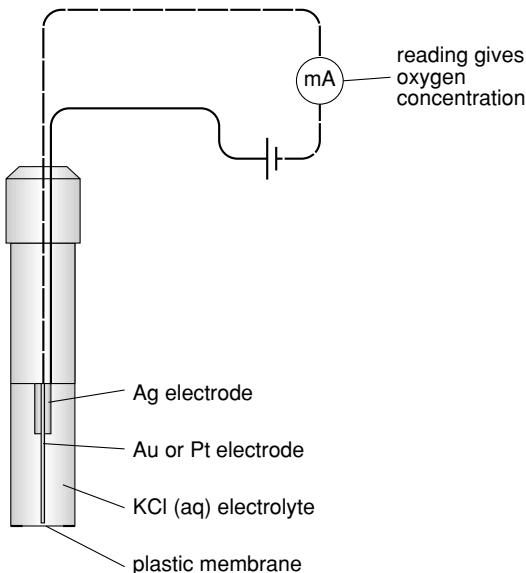
Type of water	BOD (ppm)
healthy waterway	1-6
normal discharge limit allowed by EPA	20
effluent from sewage treatment plant	20-40
raw sewage	250-350
stormwater from residential area	200-500
process industry waste (eg. chemical plant, abattoir)	500-10 000
leached water from a solid waste dump (garbage tip)	5 000-30 000

Typical BOD values.

Instrumental measurement of DO

Dissolved oxygen meters are based on electrochemical cells.

The most common type of probe uses a Au or Pt electrode and a Ag electrode in a KCl(aq) electrolyte solution. The voltage applied between the Au or Pt and Ag electrodes does not cause electrolysis until oxygen reaches the electrolyte solution. The electrodes and electrolyte are separated from the water being sampled by a plastic membrane that oxygen can diffuse through. The amount of electrolysis is proportional to the amount of oxygen. The DO level is measured by a milliammeter.



In another type of sensor an oxygen sensitive electrode connected to a reference electrode changes voltage according to the DO level.
A millivoltmeter scale is used to measure the DO level.



Justify why one of these dissolved oxygen meters is called a galvanic cell while the other is called an electrolytic cell.

Check your answer.



A remote sensor of oxygen levels that can send information to mobile phones has been developed by CSIRO. Mining sites containing sulfide ores are often buried to reduce exposure to oxygen which can oxidise sulfides to harmful sulfuric acid which contaminates water. Go to www.lmpc.edu.au/science to read more about this important development.

Common ions

Cations

Cation concentrations in the ppm and even parts per billion (ppb) range can be measured using atomic absorption spectroscopy, AAS. You will study this important technique for detecting heavy metal pollution of water in Part 2 *Chemists at work*.

Many cations form insoluble hydroxides, carbonates and sulfides. The precipitates formed can be filtered off and the mass of precipitate from a known volume of water measured. However this method may not be suitable where a number of ions are present.

The precipitate that forms could be a mixture of ions. One way of overcoming this problem is by adjustment of pH. Different hydroxides precipitate at different pHs (different hydroxide ion concentrations).

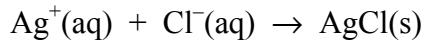
Hydroxide	pH for precipitation	pH typical for
Mg(OH) ₂	11	
	10	alkaline soil
Mn(OH) ₂	9	
	8	sea water
Fe(OH) ₂	7	river water
Zn(OH) ₂ , Cu(OH) ₂	6	rainwater
Al(OH) ₃	5	
	4	peat water
Fe(OH) ₃	3	mine water
	2	acid hot spring
	1	

Anions

The chloride ion Cl⁻ from salt is the most common ion in most natural water. Its concentration can be determined gravimetrically or by titration.

Gravimetric analysis

A known volume of water sample is concentrated by evaporation, cooled and an excess of soluble silver salt (such as AgNO₃ or AgCH₃COO) solution added.



The precipitate of AgCl is filtered off, kept in dark conditions as it is light sensitive, dried and weighed until a constant weight is obtained.



100 mL of tap water was concentrated by evaporation to about 10 mL and silver acetate solution added until no further white precipitate formed.

- 1 The silver chloride was filtered off, dried and weighed until a constant weight of 0.018g was obtained. Complete the gravimetric calculations for the molar and ppm (w/w) concentration of chloride ions:

$$0.018 \text{ g AgCl} = 0.018 \text{ g} / (107.9 + 35.45) \text{ g/mol} = \underline{\hspace{2cm}} \text{ mol}$$

Because each unit of AgCl contains one chloride ion
mol chloride = mol AgCl =

$$\begin{aligned} \text{Concentration of chloride ions} &= \underline{\hspace{2cm}} \text{ mol} / \underline{\hspace{2cm}} \text{ L} = \underline{\hspace{2cm}} \text{ mol L}^{-1} \\ &= \underline{\hspace{2cm}} \text{ g} / 1000 \text{ g} = \underline{\hspace{2cm}} \text{ ppm} \end{aligned}$$

- 2 Explain why the silver acetate solution was prepared using distilled water
-

- 3 Silver bromide AgBr and silver iodide AgI, like AgCl, are also very insoluble. A typical ionic concentration of chloride: bromide: iodide in water is in the ratio of about 1 000 000 : 1 000 : 1. Assess whether typical concentrations of bromide and iodide ions in water significantly affect the gravimetric method of determining chloride ion concentration.
-
-

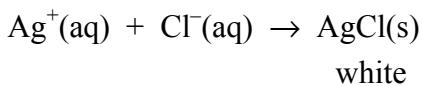


Complete Exercise 1.1: *Gravimetric determination of sulfate concentration.*

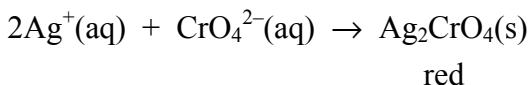
Volumetric analysis

A known volume of water sample is titrated against a soluble silver salt solution of appropriate concentration. A small amount of yellow chromate solution is added as indicator.

As the titration proceeds white AgCl precipitates out.



When all the AgCl has precipitated out silver ions react with the chromate ions producing red silver chromate.



The appearance of an orange colour due to this silver chromate marks the endpoint.



Ten drops of 0.50 M sodium chromate was added to 25.0 mL of a salt water sample which was then titrated against 0.816 M silver nitrate solution. An orange colour was seen after the addition of 20.4 mL of silver nitrate.

Calculate the molar and ppm (w/w) concentration of chloride ions:

Check your answer.

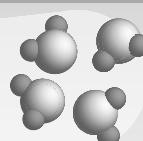
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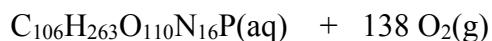
particles
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interactions

Eutrophication of waterways and the N:P ratio

The main elements in plants are C, H, O, N and P. Leaving out water these elements are in the particle or molar ratio 106:263:110:16:1 in algae. All the synthesis reactions and decay reactions that occur in algae can be summarised in an equation such as



synthesis \Downarrow \Uparrow decay



Do not attempt to learn this equation!! It simply (!!!) shows the five most important elements in photosynthetic algae and their movement between the hydrosphere and atmosphere and the biosphere.

N in organisms is mostly covalently bonded to H or C in protein molecules but in water it is mostly covalently bonded to O in nitrate ions.

P in organisms is mostly covalently bonded to O in phosphates found in DNA and ATP molecules, membranes and bones. In the environment P is also in phosphate ions which bond strongly to clay particles. Hydrogen ions secreted by plants can convert insoluble and clay bonded phosphate to soluble dihydrogen phosphate ions which plants can absorb.

Nitrogen and phosphorus in **sewage** or run off from agricultural fertiliser can over-fertilise a waterway. The ready availability of soluble nitrogen and phosphorus stimulates rapid growth of algae. The water turns green and slimy with an overpopulation of algae which soon die off and decay. The decay of carbon compounds uses up oxygen and larger organisms such as fish die from lack of oxygen. Large areas can be changed to a smelly decomposing mess releasing gases such as hydrogen sulfide and containing only decomposing organisms. An increase in nutrient content of a body of water leading to excessive growth of organisms and depletion of oxygen is known as **eutrophication**. The consequences of eutrophication can often be smelt before they are seen.

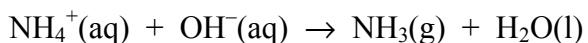
Eutrophication is most common in late summer when high light intensity and temperature stimulate growth. Certain types of photosynthetic cyanobacteria (formerly called blue-green algae) that multiply rapidly in these conditions release **toxins** poisonous to animals. In December 1991 such an incident caused about a thousand kilometres of the Darling River to be poisonous to livestock and people. Army units had to bring in special filtration plants to supply small towns with drinkable water.

Monitoring and managing N:P

Monitoring the N:P in water involves measuring total nitrogen levels (inorganic and organic nitrogen in dissolved soluble form and insoluble particle form but not nitrogen gas) and total phosphorus levels (mostly phosphate, hydrogen phosphate, dihydrogen phosphate and polyphosphate ions).

The measurements can be obtained using classical volumetric or gravimetric techniques or instrumentally by visible light absorption spectroscopy.

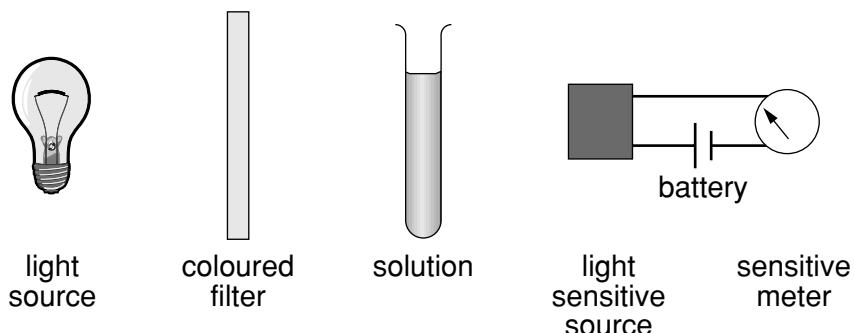
Volumetric determination of total nitrogen could involve converting nitrogen to ammonium sulfate using boiling sulfuric acid. Addition of excess alkali changes the ammonium ions to ammonia gas which is distilled off.



The ammonia is collected in, and neutralised by a known volume and concentration of excess acid. The unreacted acid is titrated against a base to determine the amount of acid which reacted with ammonia.

Gravimetric determination of phosphorus initially involves heating with a mixture of nitric acid and sulfuric acid to make sure all phosphorus is converted to phosphate. Addition of a soluble magnesium salt and ammonia solution precipitates the phosphate as insoluble magnesium ammonium phosphate-6-water. Collection and weighing of the dry precipitate enables calculation of total phosphorus.

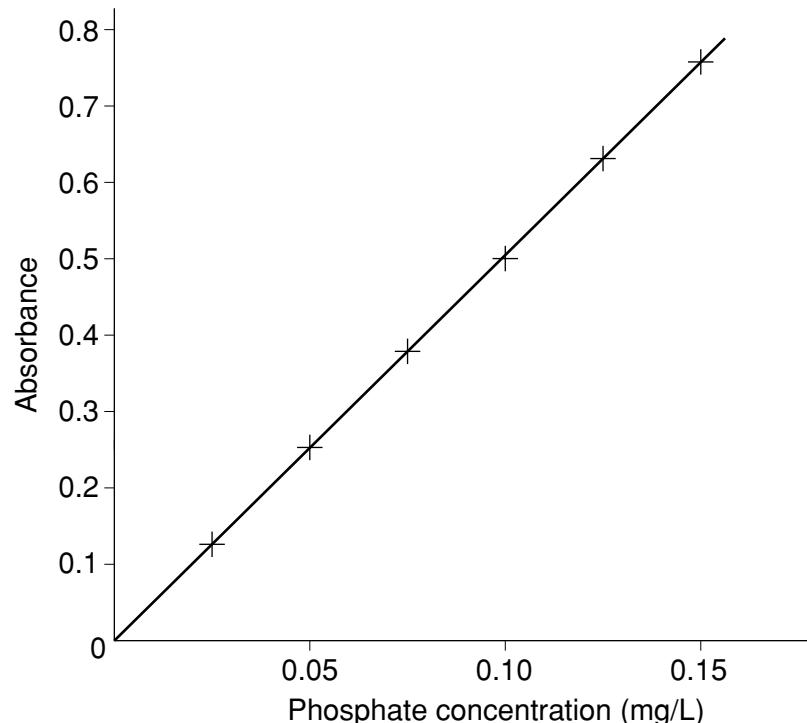
Instrumental methods involve forming a coloured solution and measuring the absorption of light of a particular colour. The measured absorbance can be compared with absorbance values obtained for solutions of known concentration.



Parts of a colorimeter.



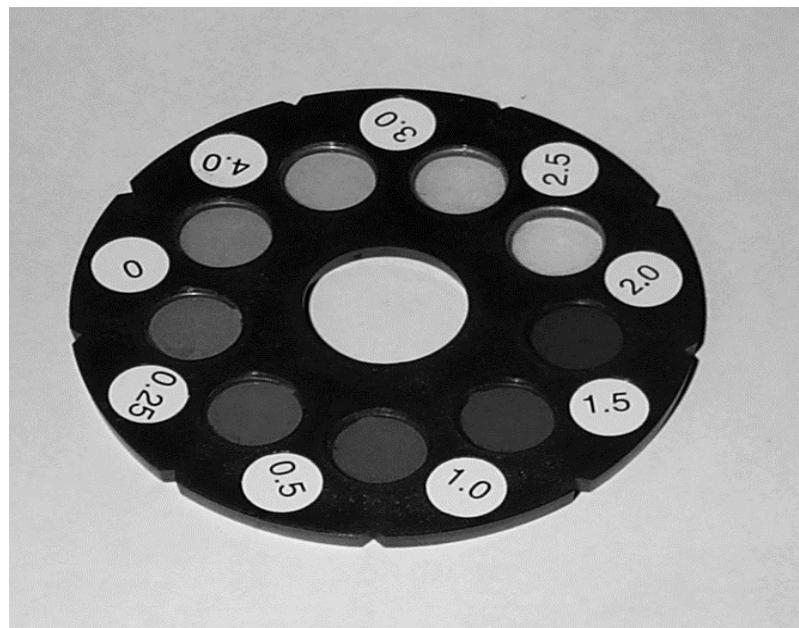
Use the graph of absorbance vs. concentration to determine the phosphate concentration in a solution with absorbance 0.62.



Alternatively the colour obtained for a solution of unknown concentration can be compared with the colours obtained for known concentrations.

The Australian and New Zealand Environment and Conservation Council (ANZECC) Guidelines (1992) recommends the following total nitrogen and total phosphate ranges:

0.10-0.75 mg/L N, 0.01-0.1 mg/L phosphate	rivers and streams
0.10-0.50 mg/L N, 0.005-0.05 mg/L phosphate	lakes and reservoirs
0.01-0.10 mg/L N, 0.005-0.15 mg/L phosphate	estuarine water
0.01-0.06 mg/L N, 0.001-0.01 mg/L phosphate	coastal waters



Comparing the colour of your unknown concentration to coloured disks enables you to estimate the concentration.

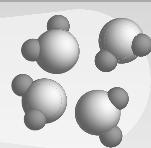


Nitrate concentration kit



Phosphate concentration kit

Management of N:P involves controlling natural sources such as water run-off and animal wastes and human sources such as sewage, fertiliser, detergents and disturbed land.

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equations
calculations**MICRO**particles
energy
interactions

Membrane filters

Filtration techniques using membrane filters with microscopic pores are increasingly being used to filter water. Use of appropriate filters can avoid the need to add chemicals to chemically treat the water supply.

Practising chemists deal with three main types of solution.

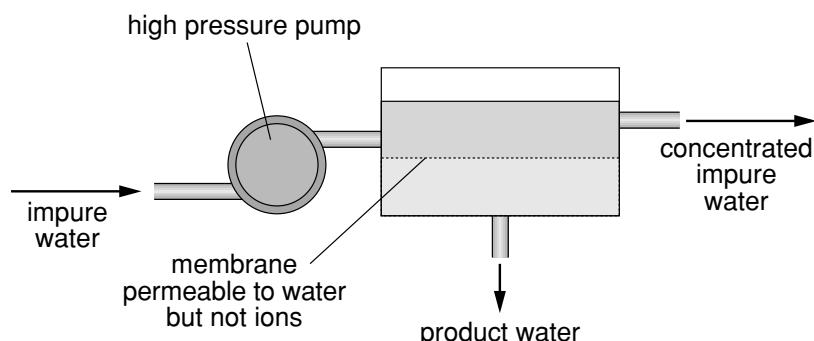
- **Suspensions** consisting of particles $> 10^{-6}$ m in diameter which can be seen with the naked eye or a light microscope; the particles can be separated from water using filters like filter paper.
- **Colloidal solutions** consisting of particles or large molecules between 10^{-9} and 10^{-6} m which can be seen with an electron microscope; they are separated from water using polymer filters made with definite sized holes.
- Solutions containing atoms, ions and small molecules between 10^{-9} and 10^{-10} m – what you have called micro level particles in this course. It is not possible to filter out these particles but it is possible to allow water to pass out of the solution in a process called reverse osmosis; pressure is applied to the solution so that water only passes through a membrane leaving a more concentrated solution of particles in water. Reverse osmosis can be used to obtain water free of heavy metal ions and all salts.

A filter paper consists of a mass of twisted cellulose fibres without definite holes (pores). A filter paper is often considered adequate if it traps at least 98% of the particles. Filter papers are suitable for separating insoluble particles such as clay suspended in water. On a larger scale thick layers of sand and gravel are used.

Microscopic membrane filters to separate colloidal particles from solution are made of polymer material with definite sized pores. They are made by dissolving a polymer in a mixture of solvents and a water soluble powder of particles of a certain size. The resulting mixture is spread over a plate, partially dried and placed in water. The solvents and powder dissolve in the water, leaving a very thin polymer sheet with definite sized microscopic pores where the water soluble particles were.

Semi-permeable membranes used in reverse osmosis are either made of cellulose acetate or a layer of polyamide attached to a layer of polysulphone. Under pressure these polymers allow passage of water molecules but not passage of most atoms, ions and other molecules.

Water under pressure is made to flow across, rather than through, the microscopic membrane filters used in microfiltration, ultrafiltration and nanofiltration. This minimises blockage of pores. Microfiltration removes protozoans (*Cryptosporidium* and *Giardia*), bacteria, colloids, some colour and some viruses. Ultrafiltration removes most colour and all viruses while nanofiltration removes hardness.



Reverse osmosis apparatus.



Use the information in the *Appendix* to decide which type of filter would be needed to separate each of the following from an impure water supply.

1 *Cryptosporidium* and *Giardia* organisms

2 Viruses

3 Water

4 Bacteria

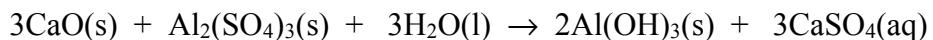
Check your answers.



Many tap filters sold in Sydney use filters with a pore size of one micron (one micrometre). Evaluate the claim that these filters remove giardia and cryptosporidium while controlling bacteria.

Check your answers.

Small clay and bacteria particles need to be brought together into larger clumps before they can be removed economically. This can be achieved cheaply by adding solid lime, CaO and solid alum, Al₂(SO₄)₃, to the water supply.



The aluminium hydroxide forms as fluffy, gel-like colloidal particles which have a large surface area. They attract and adsorb the small particles of fine clay and small bacteria. The clumps of aluminium hydroxide, fine clay and small bacteria grow so large that they settle out and can be filtered off by sand and gravel layers. The sand and gravel filters can be periodically cleaning by backwashing - reversing the direction of flow of the water and discarding the washings.

At the Sydney Olympics site

Waste water from the Sydney Olympic games site is treated at a plant which uses both microfiltration and reverse osmosis membranes.



Water Recycling And Management System (WRAMS) plant.
(Photo by Tim Reid)

The water is passed through microfiltration membranes with a pore size of 0.2 microns (micrometres = 10⁻⁶m). The Australian developed microfilter membranes can be cleaned very efficiently by pulses of compressed air.



Microfiltration membranes. (Photo by Tim Reid)



Microfiltration membranes are held in the large tubes. (Photo by Tim Reid)

Periodically the membranes are cleaned by flushing with sodium hydroxide solution. Note the MSDS for sodium hydroxide attached to the equipment.



The waste water can be passed through reverse osmosis membranes to reduce dissolved salts to about 1% of their original concentration. (Photo by Tim Reid)

Heavy metal pollution

Heavy metals are those of relatively high atomic mass generally poisonous to humans.

The National Health and Medical Research Council (NHMRC) sets the following limits for the most toxic heavy metals in food.

Metal	Limit (ppm wet weight)
mercury	0.5
cadmium	2.0
lead	2.0
copper	3.0
zinc	1 000

The **LC₅₀** (lethal concentration that kills 50% of the sample) for cadmium is about 10 ppm for fish and crabs. Tasmanian oysters and Victorian mussels have been measured with levels of 32 ppm and 9 ppm, respectively. These high results result from **bioaccumulation** of the cadmium along the smaller organisms in food chains leading to these human foods.

The recommended level for cadmium in Australian drinking water is set at 0.0 ppm.



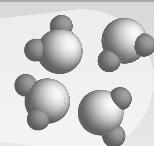
Which of these cadmium levels exceed the recommended level for Australian drinking water? (0.1 ppm, 0.05 ppm, 0.04 ppm, 0.01 ppm, 1.0 ppb)

Check your answer.

Most of the harm caused by Cd comes from its chemical similarity to Zn. Cd can replace Zn in certain enzymes, alter structure and impair function.



Complete Exercise 1.2: *Features of the local town water supply*.

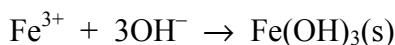
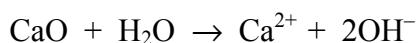
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Water filtration plants

1 Flow measurement: Measurement of the flow rate and quantity of water entering the water filtration plant (WFP) is important for determining the rates at which chemical treatments should be added.

2 **Screening:** Removes weed, small fish and debris that could foul or damage equipment such as pumps.

3 **Coagulation/Flocculation:** Addition of chemicals such as ferric chloride $FeCl_3$ solution and lime CaO so that small particles are converted to larger, heavier particles that can settle quickly.



Addition of lime raises pH, improves the buffering capacity (resistance to pH change) of the water and increases the amount of $Fe(OH)_3$ colloidal particles. The water to which chemicals have been added is mixed rapidly to distribute the chemicals evenly. The bringing together of colloidal particles is called coagulation. The slow settling out of larger particles is called flocculation.

4 Sedimentation (clarification): Slow movement of water through a long tank enables settling out of solids.

5 Filtration: Sand or coal-sand filters remove any extremely fine particles.

6 **Disinfection:** Usually chlorination to destroy bacteria and viruses not removed by sedimentation. Ammonia is added later to produce chloramines which stabilise and provide longer lasting disinfectant action

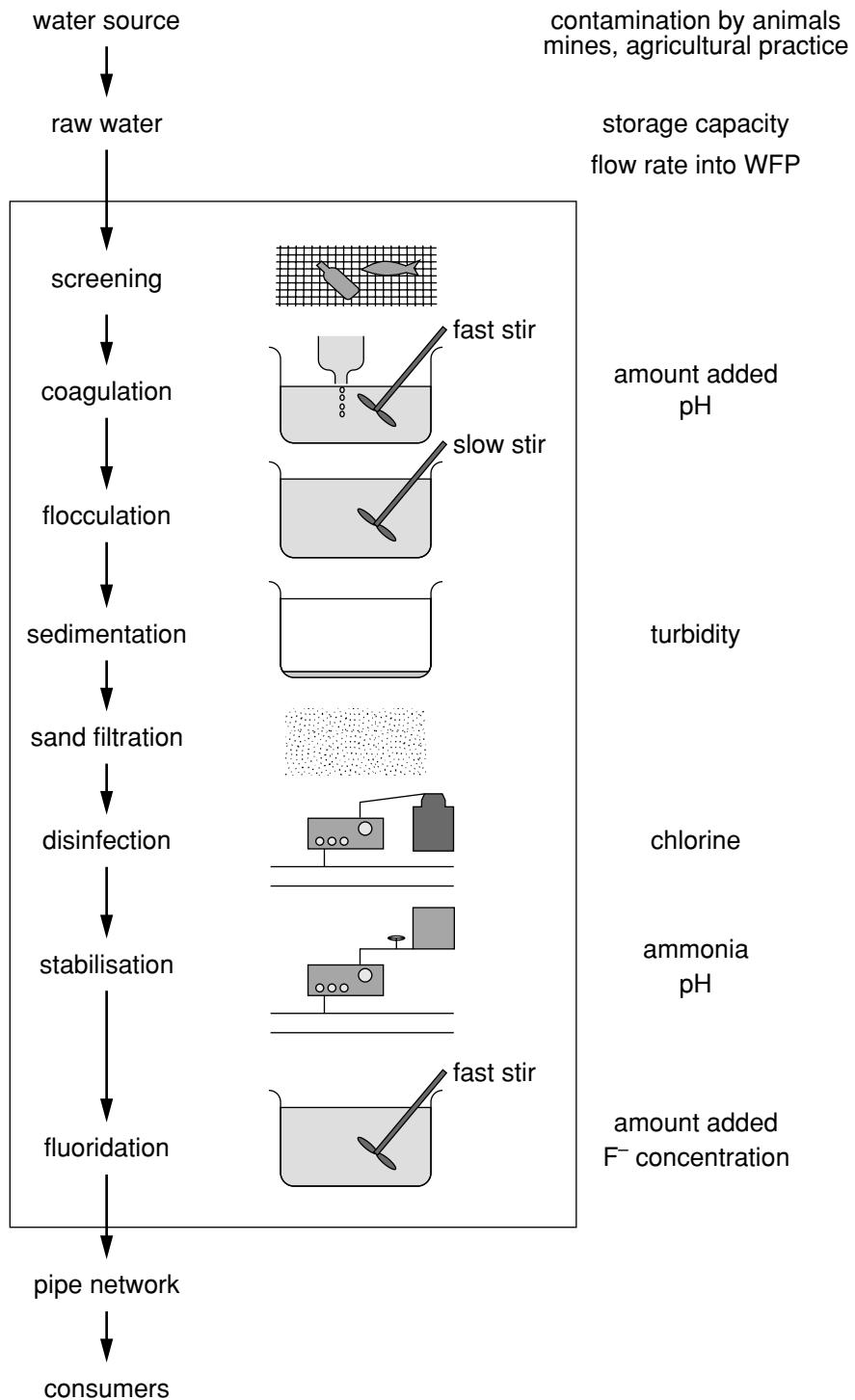
7 **Fluoridation:** Addition of a fluoride compound to about 1 ppm level to strengthen tooth enamel and reduce tooth decay particularly for children.

In some localities additional treatments carried out are:

- softening of the water by removing calcium and magnesium ions
- hardening of water by addition of lime to improve buffering capacity

- adsorption of dissolved organic materials by activated carbon
- KMnO_4 is added to oxidise manganese compounds that would otherwise pass through and cause staining of clothes and build up of scale on the inside of pipes and equipment
- polymers are added to improve flocculation.

Monitoring



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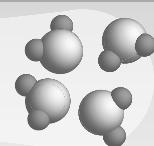
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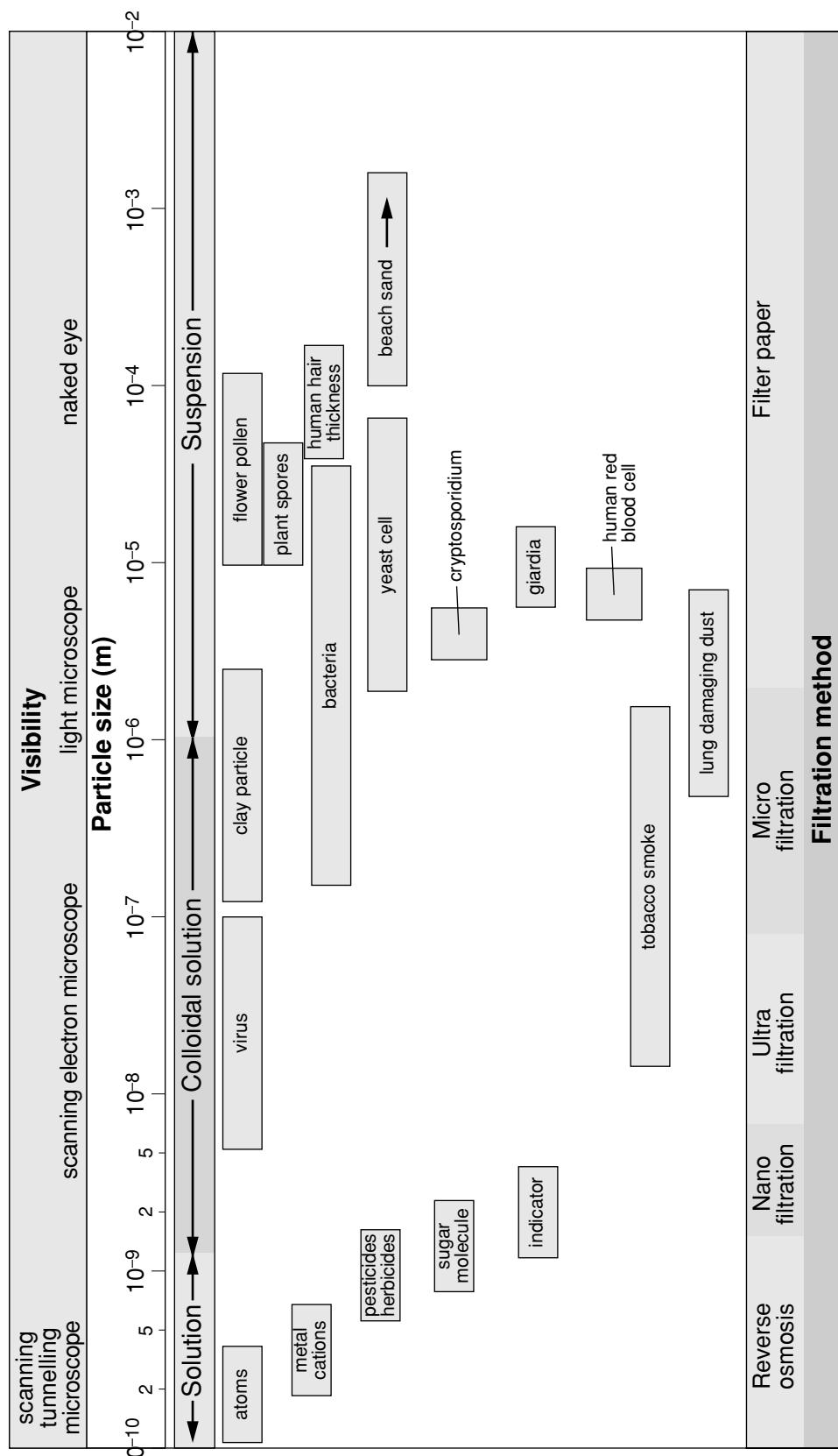
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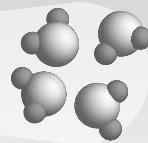
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Appendix

Filtration methods for water supplies are on the following page.



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Suggested answers

Qualitative analysis of water

- 1 Drinking water should have been filtered, treated and tested safe; another water could contain harmful microorganisms or pollution
- 2 Difference could be due to presence of a chemical or micro-organism
- 3 Boiled drinking water does not contain any dissolved gases such as those in air

What is management?

- 1 When you finished the Preliminary course you should have received a written list of assessment requirements for the HSC course. You should be able to find this information or details that you have transferred to your own diary
- 2 Look at your written notice of the nature and timing of chemistry assessment tasks (typically between three and five tasks for the HSC course).
- 3 If it took you less than a minute to find the notes you appear to be well-organised.
- 4 This could be specific equipment for this task as well as standard equipment such as calculator, rule, pencil, eraser, ink pen, paper you provide to do any assessment task.
- 5 Look at feedback on performance provided by the teacher for any previous assessment tasks. Put more effort into improving your weaknesses rather than reinforcing your strengths.

Water quality

Gases from air which can make water acidic: CO_2 , NO_2 , SO_2 , SO_3 (not CO , NO and N_2O – these are neutral non-metal oxides).

- 1 The rainwater contains no fluoride ions F
(Rainwater could contain fluoride ions but the concentration is not equal to or above 0.05 ppm (w/w). 0.0 ppm indicates the level is below 0.05 ppm. For example: Rounding down of 0.04, 0.03, 0.02 or 0.01 would all produce 0.0 while rounding up 0.05, 0.06, 0.07, 0.08, 0.09 produce 0.1.)
- 2 The rainwater could contain 0.04 ppm fluoride ions T
- 3 The seawater data must be wrong because the $\text{Na}^+:\text{Cl}^-$ in salt is 1:1 F
(The 1:1 ratio for $\text{Na}^+:\text{Cl}^-$ is a particle or mole ratio. The figures provided for sodium ions and chloride ions are weight figures. Also other salts are present in sea water that affect the amount of Na^+ and Cl^-)

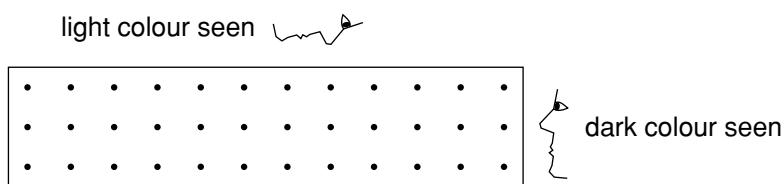
Hg mercury
 Pb lead
 Cd cadmium
 Mn manganese
 H_2S hydrogen sulfide
 CaCO_3 calcium carbonate
 F⁻ fluoride ion

Visualising a concentration of 1 ppm

KMnO ₄ concentration (ppm)	Weight of KMnO ₄ in each drop(g)
10 000	0.0005 = 500 micrograms
100	0.000005 = 5 micrograms
1	0.00000005 = 0.05 micrograms

Conclusion: It is possible to prepare a 1 ppm solution of KMnO₄ in water and see the colour of the permanganate ions.

- 1 Diagram comparing thickness of solution viewed and number of particles.



- 2 Dissolve a very small but accurately measured amount of the chemical in a large accurately measured volume of solvent.

A small volume of the solvent contains an extremely small mass of the chemical. If this is measured out and the solvent allowed to evaporate an extremely small mass of chemical is left behind.

Thus evaporation of one drop of 1 ppm KMnO₄ solution would leave behind 0.05 micrograms of KMnO₄.

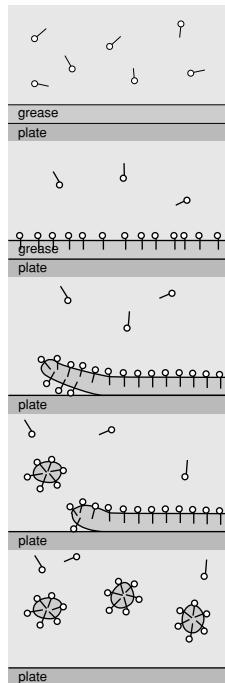
Insoluble solids

- 1 Concentration of insoluble solid in g/L = $(1.71 - 0.82) \text{ g} / 0.500 \text{ L} = 0.89/0.500 = 1.8 \text{ g/L}$
- 2 Calculate the concentration of insoluble solid in mg/L = ppm.
 $1.8 \text{ g/L} = 1\ 800 \text{ mg/L} = 1\ 800 \text{ mg/kg of water} = 1\ 800 \text{ mg} / 1\ 000\ 000 \text{ mg} = 1\ 800 \text{ ppm (w/w)}$

Total dissolved solids (TDS)

- 1 Insoluble solid must be filtered out otherwise the insoluble solid will be part of the weight measured as dissolved solid.
- 2 Weight of dissolved solid = $251.13 - 250.76 = 0.37 \text{ g}$
Volume of water = 1 000 mL
Weight of water = $1\ 250.28 - 250.76 = 999.52 \text{ g}$
- 3 $(\text{w/w}) = 0.37/999.52 = 0.00037 = 370 \text{ ppm}$
 $(\text{w/v}) = 0.37/1\ 000 = 0.00037 = 370 \text{ ppm}$

Chemical hardness



Soap solution is added to the greasy plate

Soap ions arrange themselves with the hydrophobic carbon chain in grease and the hydrophilic polar group in water

Soap ions help separate grease from the plate

With some agitation small globules of oil are lifted away from the plate.

Soap ions surround oil globules preventing them from joining together and keeping them suspended in the soapy water which turns darker

Gravimetric method precipitating carbonates

Formula mass of $\text{CaCO}_3 = 40.08 + 12.01 + 3 \times 16.00 = 100.09$ g/mole

$3.48 \text{ g} = 3.48 / 100.09 = 0.0348 \text{ mol CaCO}_3$

each CaCO_3 contains one calcium ion thus concentration of Ca^{2+}

$= 0.0348 \text{ mol} / 4.00 \text{ L} = 0.00869 \text{ mol L}^{-1}$

$0.00869 \text{ mol Ca}^{2+} = 0.00869 \times 40.08 \text{ g} = 0.348 \text{ g}$

$1.00 \text{ L of water} = 1000 \text{ g}$

$0.00869 \text{ mol L}^{-1} \text{ Ca}^{2+} = 0.348 \text{ g} / 1000 \text{ g} = 348 \text{ ppm}$

Soap titration method

Because the hard water solution required $15.0 / 5.00 = 3$ times as much soap solution it is three times as concentrated, that is $3 \times 100 = 300$ ppm CaCO_3 .

Dissolved oxygen (DO)

$$\text{mol thiosulfate} = 5.40 \times 10^{-3} \times 0.0500 = 0.000270$$

$$\text{mol oxygen} = 1/4 \times 0.000270 = 0.0000675$$

$$\begin{aligned}\text{Molar concentration of oxygen} &= 0.0000675 \text{ mol / 0.500 L} \\ &= 0.000135 \text{ mol L}^{-1}\end{aligned}$$

$$\text{mol oxygen in each litre} = 0.000135$$

$$\text{mass of oxygen in each litre} = 0.000135 \times 32.0 \text{ g} = 0.00432 \text{ g}$$

$$\begin{aligned}\text{ppm of oxygen} &= \text{mass of oxygen in one litre / mass of one litre of water} \\ &= 0.00432 \text{ g} / 1000 \text{ g} \\ &= 4.32 \text{ ppm}\end{aligned}$$

- 1 To prevent oxygen production by any photosynthetic organisms
- 2 The amount of oxygen that can dissolve decreases with temperature rise.

Instrumental measurement of DO

The meter that has a voltage applied and measures current is an electrolytic cell as electrical energy from the applied voltage is used to produce chemical change. The meter that measure voltage generated between two electrodes is a galvanic cell as chemical change is producing a voltage.

Gravimetric analysis

$$1 \quad 0.018 \text{ g AgCl} = 0.018 \text{ g} / (107.9 + 35.45) \text{ g/mol} = 0.00013 \text{ mol}$$

Because each unit of AgCl contains one chloride ion

$$\text{mol chloride} = \text{mol AgCl} = 0.00013$$

$$\begin{aligned}\text{Concentration of chloride ions} &= 0.00013 \text{ mol / 0.100 L} \\ &= 0.0013 \text{ mol L}^{-1}\end{aligned}$$

$$= 0.0013 \times 35.45 \text{ g / 1000 g} = 50 \text{ ppm}$$

- 2 Distilled water was used to prepare the solution because chloride ions in tap water would precipitate AgCl turning the solution cloudy white.
- 3 Because bromide concentrations are about one-thousandth chloride concentrations they would only have a significant effect if measurements were made to more than three significant figures.

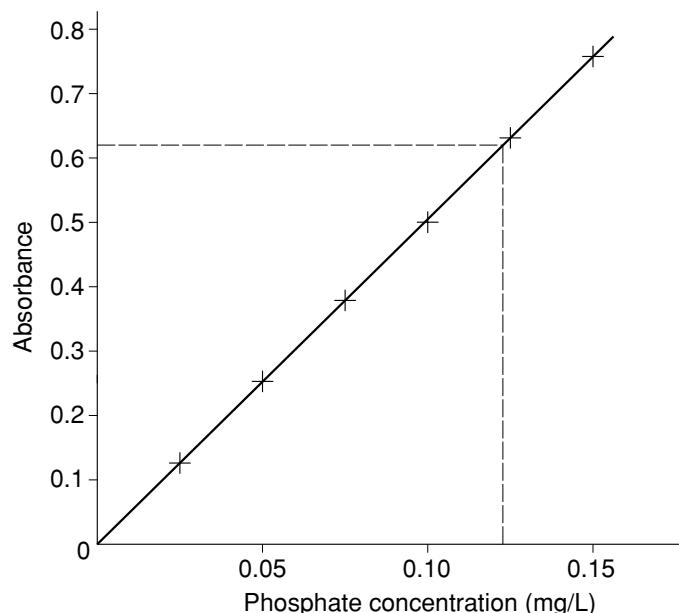
Volumetric analysis

20.4 mL of 0.816 M silver nitrate solution contains $20.4 \times 10^{-3} \times 0.816$
 $\text{mol Ag}^+ = 0.0166 \text{ mol Ag}^+ = \text{moles of Cl}^-$

molar concentration of $\text{Cl}^- = 0.0166 \text{ mol} / 0.0250 \text{ L} = 0.666\text{M}$

$= 0.666 \times 35.45 \text{ g/L} = 23.6 \text{ g/L} = 23\,600 \text{ mg/L} = 23\,600 \text{ ppm.}$

Monitoring and managing N:P

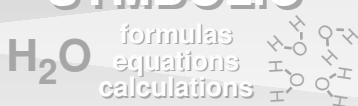
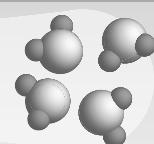


Membrane filters

- 1 Cryptosporidium and Giardia organisms could be filtered out by suitable paper filters
- 2 Viruses could be filtered out by nanofilters.
- 3 Water could pass through a semi-permeable membrane used in reverse osmosis.
- 4 Bacteria could be filtered out by microfilters – from an impure water supply.

A one micron (10^{-6} m) filter should trap all particles larger than one micron – giardia and cryptosporidium but control only larger bacteria, not smaller bacteria. The claim appears true.

The recommended level for Cd in Australian drinking water is 0.0 ppm. Any level below 0.05 ppm such as 0.04 ppm, 0.01 ppm and 1.0 ppb is closer to 0.0 ppm than 0.1 ppm and so could be used as Australian drinking water.

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energy
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Exercises – Part 1

Exercises 1.1 to 1.2

Name: _____

Exercise 1.1: Gravimetric determination of sulfate concentration

Sulfate concentration can be determined gravimetrically by first adding acid to react with carbonate ions then excess barium ions, filtering off, drying and weighing the $BaSO_4$ precipitate.

- 1 Barium carbonate is insoluble. Adding acid before adding barium ions prevents $BaCO_3$ precipitating with the $BaSO_4$. Write a balanced equation for the reaction in which H^+ ions destroy a carbonate ion releasing a gas.

- 2 Explain why the acid added in this determination must not be sulfuric acid.

- 3 Write an equation for the precipitation of $BaSO_4$

- 4 If 0.233 g of $BaSO_4$ precipitates from 1.00 L of water, what was the molar concentration of sulfate ions?

Exercise 1.2: Features of the local town water supply

Gather, process and present information on the following features of your local town water supply:

Feature	Information
Catchment area (land bounded by hills or mountains from which surface or ground water flows)	
Possible sources of contamination in this catchment	
Chemical tests available to determine levels and types of contaminants	
Physical processes used to purify	
Chemical processes used to purify	
Chemicals added to the water and the reasons for these additions	

Chemistry

HSC Course

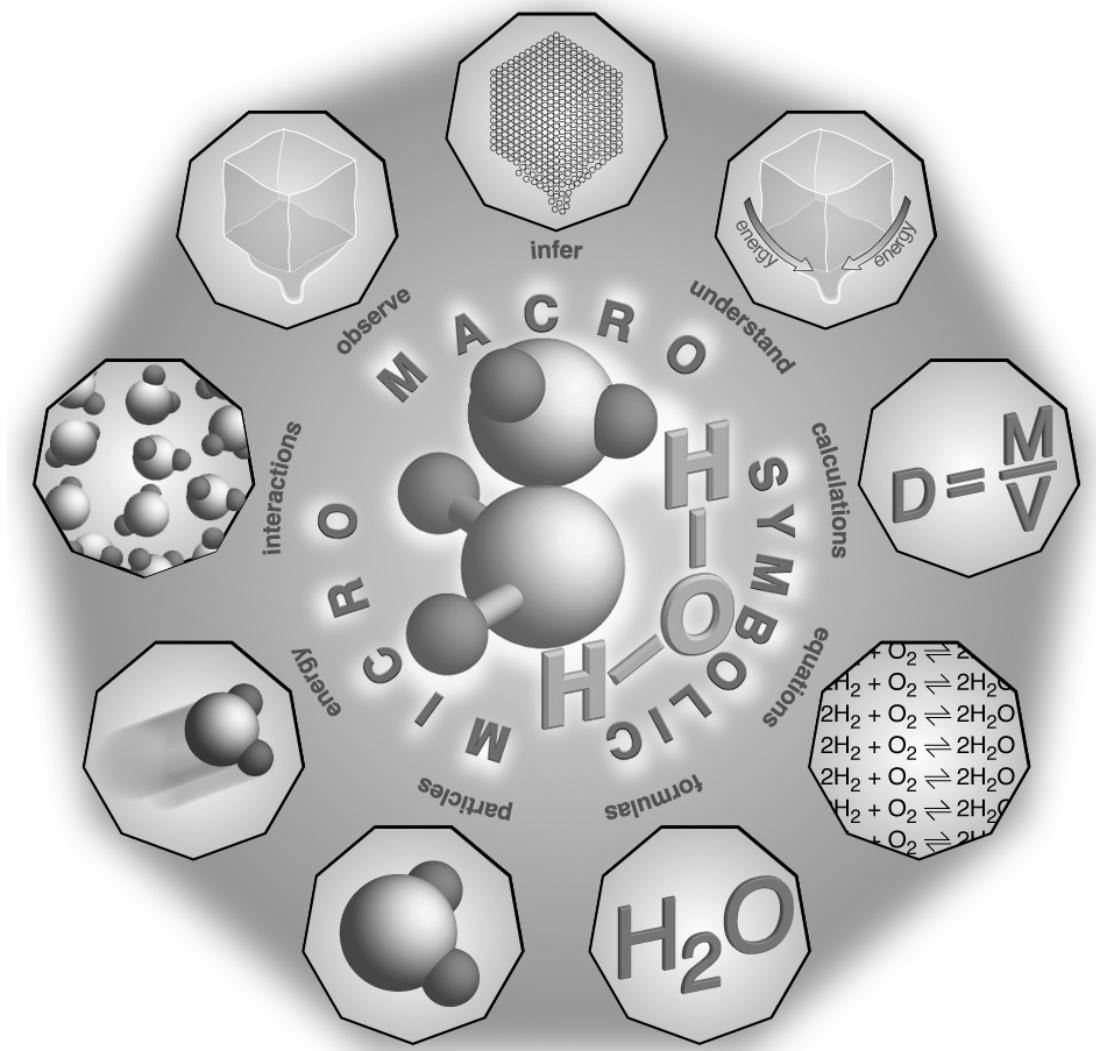
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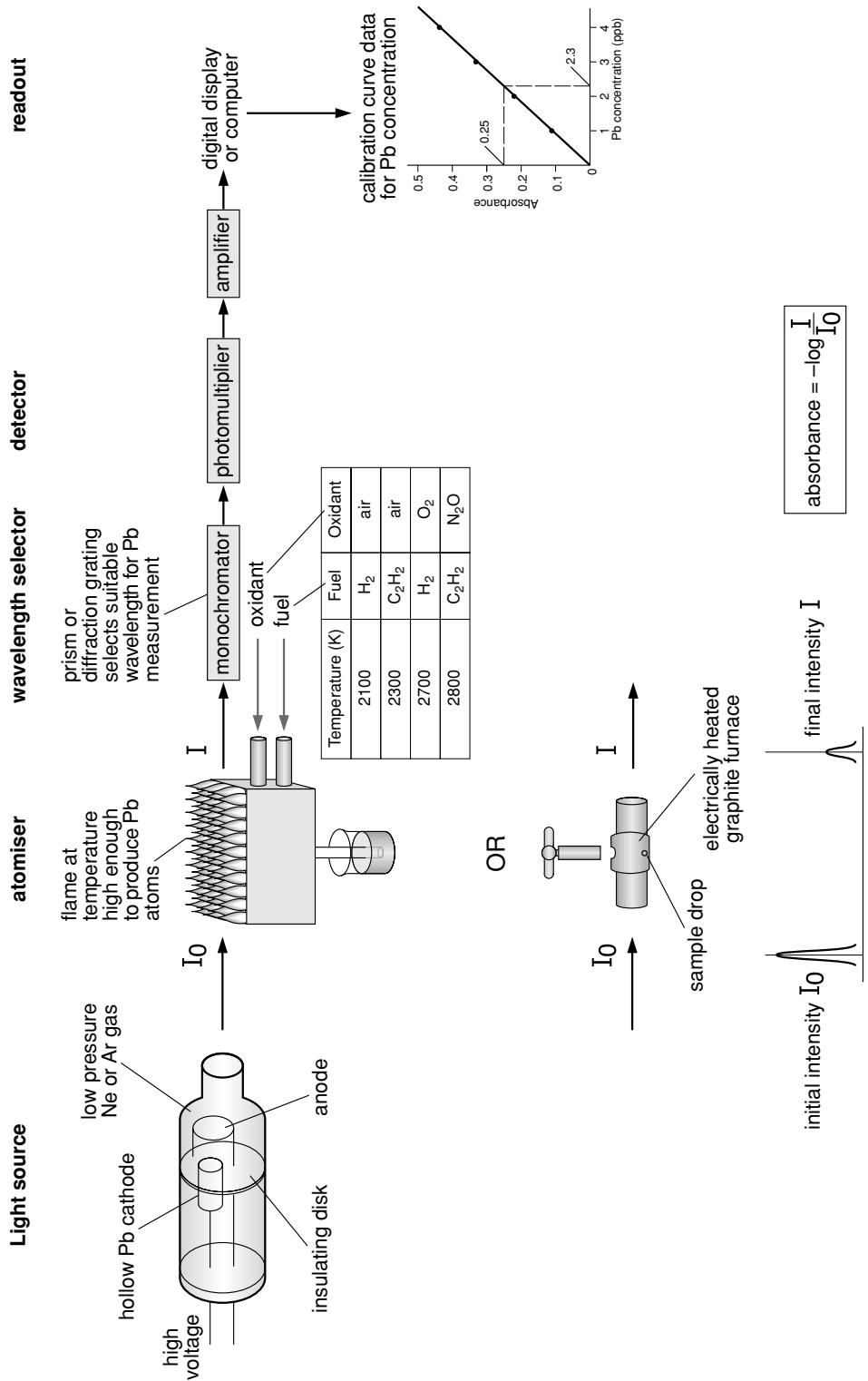
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Chemical monitoring and management

Part 2: Chemists at work





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energy
interactions

Contents

Introduction	2
Chemists in Australia.....	3
Different types of chemists	4
Atomic absorption spectroscopy	6
Chemists who use AAS	8
Understanding a chemistry job description	9
Calibration – a principle used by analytical chemists	10
Trace elements and AAS	11
Chemical principles	12
Monitoring and managing modern internal combustion engines	14
Suggested answers.....	19
Exercises – Part 2	23

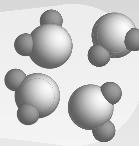
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calculations



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Introduction

The Royal Australian Chemical Institute (RACI) is the qualifying body in Australia for professional chemists. The RACI promotes the science and practice of chemistry. Of the nearly 10 000 members the two largest divisions are analytical chemistry (25%) and industrial chemistry (15%). Analytical chemists apply chemical and physical methods to qualitatively detect specific chemicals and quantitatively measure the amount of chemicals. Much of the work of industrial chemists involves monitoring the reactants and products of reactions and managing reaction conditions

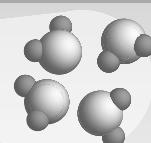
In Part 1 you will be given opportunities to learn to:

- outline the role of a chemist employed in a named industry or enterprise, identifying the branch of chemistry undertaken by the chemist and explaining a chemical principle that the chemist uses
- describe the use of atomic absorption spectroscopy (AAS) in detecting concentrations of metal ions in solutions and assess its impact on scientific understanding of the effects of trace elements
- identify the need for collaboration between chemists as they collect and analyse data
- describe an example of a chemical reaction such as combustion, where reactants form different products under different conditions and thus would need monitoring.

In Part 1 you will be given opportunities to:

- gather, process and present information from secondary sources about the work of practising chemists identifying:
 - the variety of chemical occupations
 - a specific chemical occupation for more detailed study
- gather, process and present information to interpret secondary data from AAS measurements and evaluate the effectiveness of this in pollution control.

Extracts from *Chemistry Stage 6 Syllabus* © Board of Studies NSW, originally issued 1999. The most up-to-date version is to be found at http://www.boardofstudies.nsw.edu.au/syllabus99/syllabus2000_list.html

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Chemists in Australia

Members of the Royal Australian Chemical Institute (RACI) can be:

- Students undertaking a science or engineering course majoring in chemistry, chemical engineering, biochemistry or some other specialised branches of chemistry, materials science, food science and textile technology
- Associates with an interest in chemistry but without formal qualifications
- Associate (Technician) ATRACI with a TAFE (Technical and Further Education) or diploma or equivalent qualification in chemistry
- Associate (Graduate) GRACI who possess an appropriate university qualification and are proceeding to higher degrees or practising in industry, education or government services. GRACI are eligible for rates of payment prescribed by the Professional Scientist's Award
- Member Chartered Chemist MRACI CChem obtainable by GRACIs after at least four years of approved professional experience
- Fellow Chartered Chemist FRACI CChem recognised as being in a position of eminence. Election to this grade is based on academic qualifications and honours, experience and status, creative achievement in chemistry, responsibility and contribution to chemical science.

Satisfactory achievement in this Chemistry Stage 6 course can lead to chemistry related courses such as medical studies, paramedical studies, pharmacy, agriculture as well as the science and engineering courses in TAFE and universities that can qualify for membership of the RACI.

Information about post-school opportunities provided by Chemistry Stage 6 can be found on page 92 of the syllabus.



A pharmacy is sometimes called a chemist's shop and the pharmacist is sometimes called the chemist. Use information from a dictionary or an internet search engine to explain the difference between a pharmacist and a professional chemist as recognised by the RACI.

Check your answers.

Different types of chemists



Chemists in the Royal Australian Chemical Institute are in thirteen national divisions.

RACI division	% of total members	Example of a study area
Analytical	25	
Industrial	15	
Organic	13	
Environment	10	
Polymer	8	
Biomolecular	7	
Inorganic	5	
Chemical education	5	
Physical	4	
Colloid and surface science	3	
Cereal	2	
Electrochemistry	2	
Solid state	1	

Place each of the following study areas in the appropriate space:

‘chemical batteries, improving detergent action, learning of chemistry, measurement of concentrations, minerals, N:P in water, petrochemicals, properties of plastics, physical properties and changes, protein in grains, protein structure, production efficiency, silicon solar cells and chips’

Check your answers.

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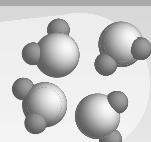
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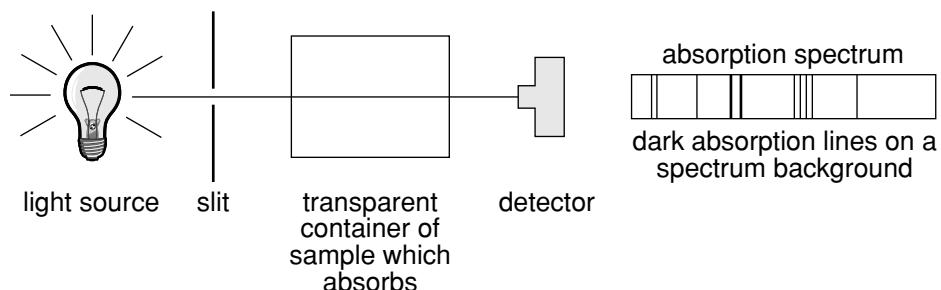
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energy
interactions

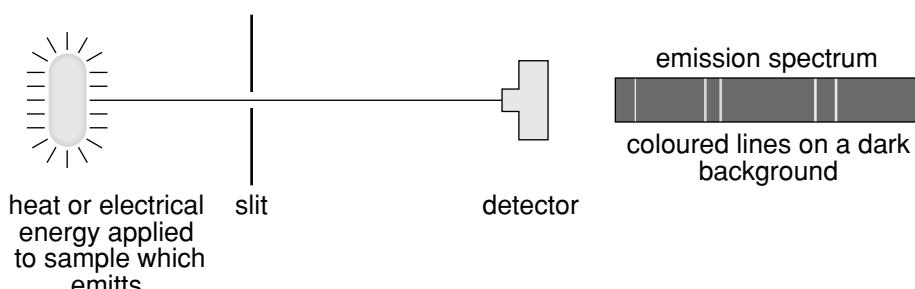


Atomic absorption spectroscopy (AAS)

CSIRO scientist Alan Walsh wondered why most measurement of molecules used absorption of light while most measurement of atoms used emission of light.



Absorption spectroscopy.



Emission spectroscopy.

Working in his Melbourne garden in 1952 Alan Walsh realised there was a way of measuring small concentrations of metallic elements more accurately using absorption rather than emission of light. His idea, followed up by years of development led to worldwide application of the technique known as atomic absorption spectroscopy (AAS).

AAS has even been called the major advance in analytical chemistry in the twentieth century! Nearly 50 years later AA spectrometers can be found in hospitals, factories and laboratories throughout the world and approximately one third of the world's equipment is made in Australia.

Analytical chemists can use AAS to detect as low as ppb quantities of metals and some solid non-metals in soils, minerals, blood, urine, pharmaceuticals, engine oils, water and drinks. The technique vastly increased scientists' ability to measure environmental concentrations.

The technique uses a lamp containing a hollow cathode made of the element being analysed. A hollow cathode lead lamp emits wavelengths absorbed by lead atoms only. If any lead atoms are in the sample being analysed they will absorb this light from the lead lamp. The amount of light absorbed by any lead atoms in the sample is proportional to the number of lead atoms in the sample.

The sample is in liquid form. Two systems can be used to produce atoms able to absorb light:

- **aspiration** draws the liquid into a flame of a fuel/oxidant mixture
- a drop of liquid is heated electrically inside a graphite tube.

The more recent development of graphite furnaces has improved detection limits for most metals so they are now 100 to 1000 times lower than AAS using a flame. Using a graphite furnace the level of detection for some metals has gone from ppm to ppb!



Study the diagram showing atomic absorption spectroscopy on the inside cover of this part. Use the information provided in the diagram and in the table below to decide whether the lead analysis was carried out using flame AAS (FAAS) or graphite furnace AAS (GFAAS). Justify your answer.

Metal	Wavelength (nm)	Fuel/oxidant	Typical working range (ppm)	Lowest detection limit (ppm)
cadmium	229	C ₂ H ₂ /air	0.05-2	0.002
chromium	358	C ₂ H ₂ /air	0.2-10	0.02
lead	283 or 217	C ₂ H ₂ /air	1-20	0.05
vanadium	319	C ₂ H ₂ /N ₂ O	2-100	0.2

Check your answers.

Chemists who use AAS

Atomic absorption spectroscopy is a technique, an atomic absorption spectrometer is the instrument used while an atomic absorption spectroscopist is a person.

An atomic absorption spectroscopist could be:

- a laboratory technician carrying out routine analysis and largely concerned with smooth operation of the equipment
- a chemist concerned with checking on satisfactory sample collection methods, satisfactory operation of the equipment and interpretation of the results
- a research chemist who oversees the work of the technician and chemist but is more concerned with developing new applications or understandings from the results.

Collaboration means working together. Collaboration is important between these different chemists and other technical and scientific workers such as the collector of samples, the technician from the equipment manufacturer or any scientist who uses the results in coming to a conclusion. Collaboration is needed between the chemists who collect data and the chemists who analyse data to achieve reliable (consistent) and valid (true) results and conclusions.



Explain, with examples, why collaboration is so important between the collectors of water samples and the laboratory analysers of the water samples.

Check your answers.

Understanding a chemistry job description



Read the description for this chemistry position and its supplementary notes. Use this information to answer the questions that follow.

Research Fellow

Institute for Biomolecular Science/Chemistry

A post-doctoral fellowship is available for an exciting AMRAD supported project on the design and synthesis of novel antibacterials targetted at the antibacterial resistance problem (1 year appointment – Reference 20-180). Applicants must have completed a PhD in a relevant area including experience in organic synthesis with the ability to work as part of a team and with good oral and written communication skills. Experience in computer-based molecular design and HPLC would be desirable. This is a re-advertised position and previous applicants will still be considered. Annual salary up to \$47,228.

AMRAD is an Australian biotechnology research and development company.

HPLC is high performance/pressure liquid chromatography.

- 1 List essential criteria for this position.

- 2 List two criteria which are not essential but would be desirable.

- 3 List the two criteria which indicate the importance of collaboration.

- 4 Are the criteria involving collaboration essential or only desirable?

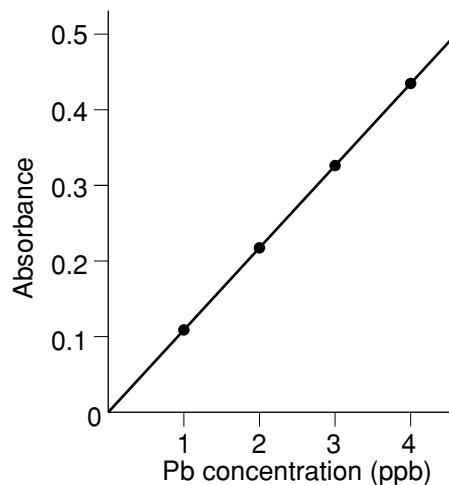
Check your answers.

Calibration - a principle used by analytical chemists

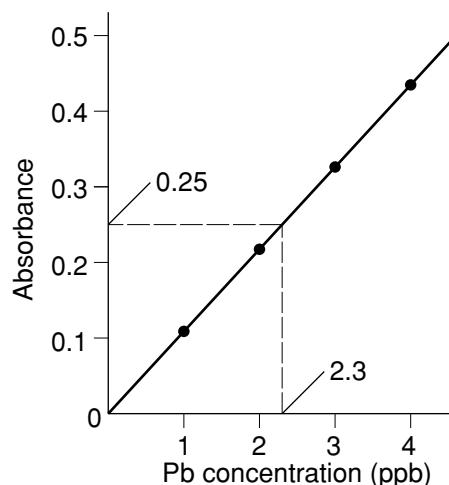
The **absorbance** – amount of light of a certain wavelength absorbed by a substance – is proportional to the number of molecules/atoms/ions of that substance in a sample. As the concentration of the substance increases the amount of light absorbed will increase.

If standard solutions of different concentrations of the substance are prepared the absorbance for each standard solutions can be measured.

A **calibration curve** can be drawn using such measurements.



If the absorbance of a sample solution is measured the calibration curve can be used to measure the sample's concentration as shown below.



Trace elements and AAS

The main elements needed by organisms are C, H, O and N.

Nutrient elements are needed in smaller amounts eg. P, Ca, S, Na, K, Cl.

Trace elements are needed in minute traces eg. Cu, Se, Zn, B, Mo, Mn.

Until the development of AAS it was very difficult to measure the very low amounts of trace elements in Australian soils.

European settlers in coastal regions of South Australia and parts of coastal Western Australia found that lush pasture could not support healthy animals. Movement inland enabled the sheep and cattle to recover. When a natural mineral containing iron was fed to the sheep and cattle they could survive on the coast. Soil iron deficiency was believed to be the cause of the problem. However measurements with AAS showed that in fact cobalt deficiency was the cause. The natural mineral had contained minute traces of cobalt needed in the animal's diet.



In parts of Australia arid land can now grow legume crops thanks to the application of about 100 g of molybdenum per hectare. A hectare is an area 100 m by 100 m.

- 1 Calculate the amount of molybdenum needed per square metre.

- 2 If this amount of molybdenum was uniformly mixed into 100 kg of soil what would the concentration of molybdenum be in ppm by weight?

Check your answers.

MACRO

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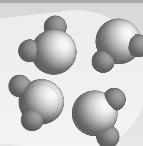


SYMBOLIC

H_2O formulas
equations
calculations



formulas
equations
calculations



MICRO

particles
energy
interactions

Chemical principles

Here are some chemical principles from the Stage 4 science syllabus.

- Matter is made up of particles that are moving and interacting.
- Changes in particle movement are related to changes in amount of energy possessed by the particles.
- Changes in pressure are related to changes in frequency of particle collisions.
- Changes in state are related to changes in motion of particles as energy is removed or added.
- Chemical reaction is taking place if a new substance appears or the original substance disappears.

Here are some chemical principles from the Stage 5 science syllabus.

- An atom is the smallest unit of an element.
- A new compound is formed by rearranging atoms.
- An atom can combine with other atoms by gaining, losing or sharing electrons.
- Properties of different substances can be explained in terms of their subatomic structure.
- Forces of cohesion, adhesion and repulsion may exist between particles.



Write either analytical, industrial, electrochemistry, environmental or biomolecular after each Stage 6 Chemistry principle listed below to describe the branch of chemistry using that principle.

Stage 6 Chemistry principles	Branch
oxidation of chemical species is due to loss or gain of electrons	
radiation from radioactive elements can be detected by an instrument	
concentrations of reactants and products in a mixture at equilibrium will alter so as to counteract any change in concentration, temperature or gas pressure	
the properties of a biopolymer depend on its structure	
particles can absorb or emit electromagnetic radiation	

Check your answers.



Complete Exercise 2.1.

MACRO
observe
infer
understand

SYMBOLIC
 H_2O formulas
equations calculations

MICRO
particles
energy
interactions

Monitoring and managing modern internal combustion engines

Since the mid 1980s all new petrol engine cars in Australia have been required to use unleaded petrol and catalytic converters. Unleaded petrol does not damage the platinum (Pt), palladium (Pd) and rhodium (Rh) catalysts. These catalysts can change harmful CO, hydrocarbons (HC) and NO_x exhaust gases to CO₂, H₂O and N₂.



Explain why the following gases are considered harmful to humans and/or the environment:

- carbon monoxide

- hydrocarbons

- nitrogen oxides

Check your answers.

Monitoring using an oxygen sensor in the exhaust manifold and a management system controlled by an electronic control unit (ECU) improves the efficiency of engines and reduces harmful exhaust gases.

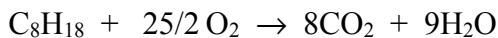
The electronic control unit aims to achieve a stoichiometric ratio of air:fuel. That is, just enough air to completely combust the hydrocarbon to carbon dioxide and water. Normally 14.7 kg of air is required to completely combust 1 kg of petrol.

The air:fuel ratio is called lambda λ . Lambda, λ is given the value 1 when combustion is most efficient and releases the most heat energy. The oxygen sensor used to monitor this is also called the lambda sensor.

A mixture with an air:fuel ratio of $< 14.7:1$ (w/w) has $\lambda < 1$ and is called rich.

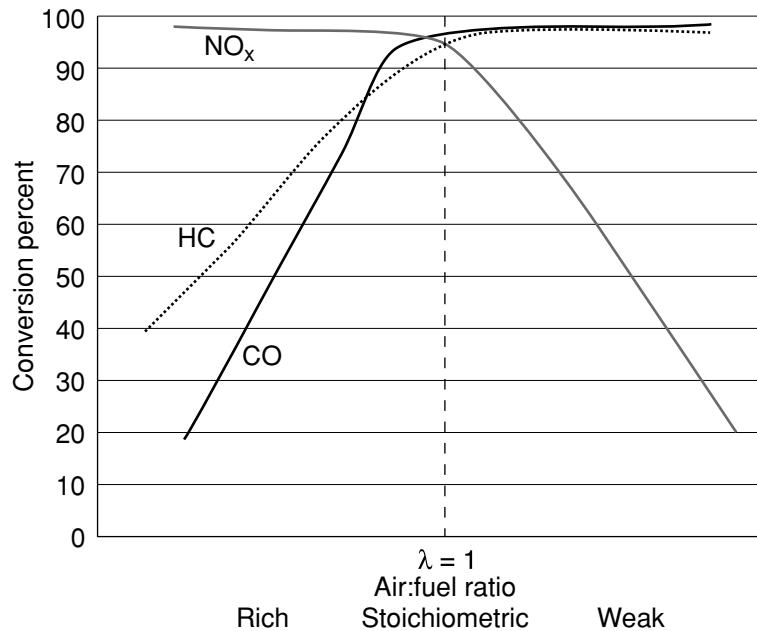


Here are two equations for combustion of a typical petrol hydrocarbon. Assess which equation represents $\lambda = 1$.

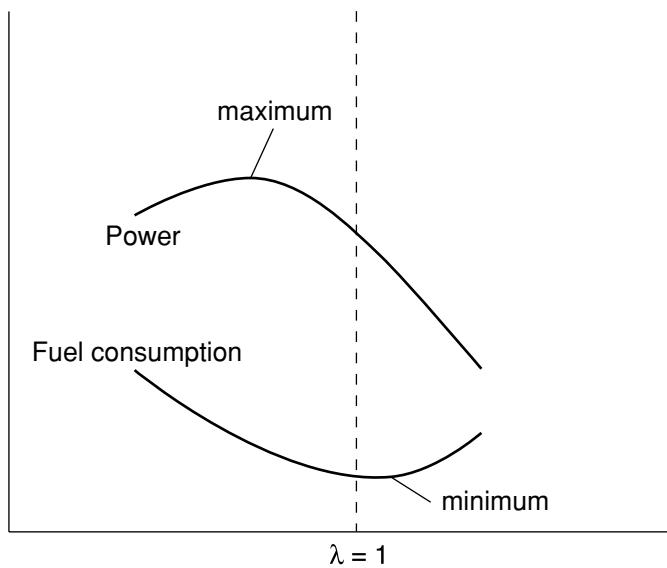


Check your answer.

The catalytic converters used in Australia are called three-way converters as they convert all three harmful gases (CO, HC and NO_x) simultaneously. The metals used as catalysts are very expensive but only cost \$5–10 per converter. They are deposited in a thin layer on the surface of ceramic in honeycomb shape or pellet form.



Graph showing how $\lambda = 1$ achieves greatest conversion of harmful gases.

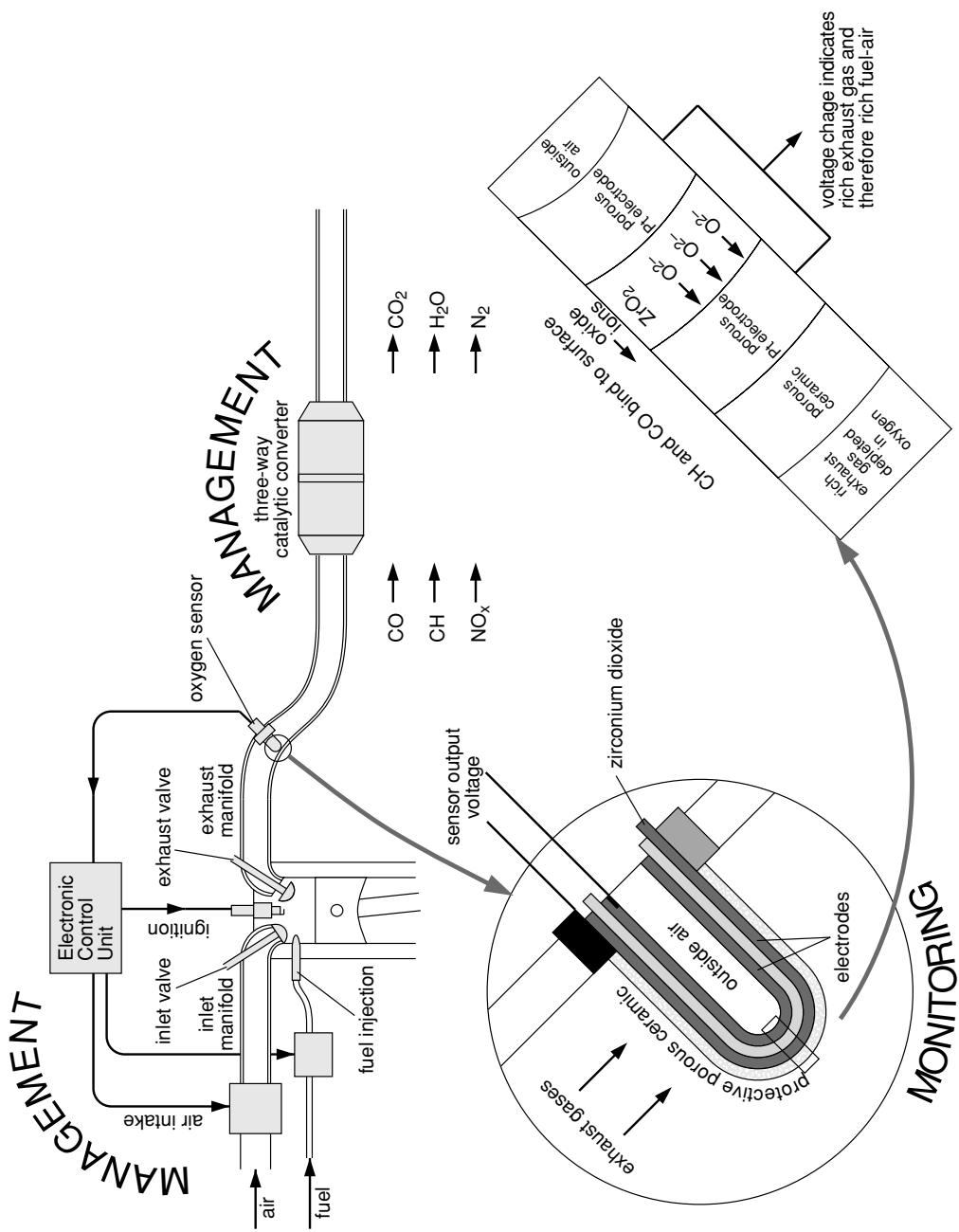


Graph showing how $\lambda = 1$ represents a compromise between maximum power and minimum fuel consumption

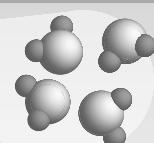


Try to locate the oxygen sensor (lambda sensor), catalytic convertor and electronic control unit on a petrol engine car no more than 15 years old. They may be easier to locate on cars built between 1985 and 1995. More recent models often have plastic parts covering over these units.

Study the diagram on the following page before you go looking.



Complete Exercise 2.2.

MACROobserve
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understand**SYMBOLIC** H_2O formulas
equations
calculations**MICRO**particles
energy
interactions

Suggested answers

Chemists in Australia

A pharmacist or pharmaceutical chemist prepares and dispenses drugs and medicines using prescriptions from medical doctors or veterinarians. Most pharmacists work in shops or hospitals. Professional chemists work with a wide range of chemicals; they can be qualified in the isolation, purification, designing and production but not dispensing of drugs and medicines.

RACI division	% of total members	Example of a study area
Analytical	25	<i>measurement of concentrations</i>
Industrial	15	<i>production efficiency</i>
Organic	13	<i>petrochemicals</i>
Environment	10	<i>N:P in water</i>
Polymer	8	<i>properties of plastics</i>
Biomolecular	7	<i>protein structure</i>
Inorganic	5	<i>minerals</i>
Chemical education	5	<i>learning of chemistry</i>
Physical	4	<i>physical properties and changes</i>
Colloid and surface science	3	<i>improving detergent action</i>
Cereal	2	<i>protein in grains</i>
Electrochemistry	2	<i>chemical batteries</i>
Solid state	1	<i>silicon solar cells and chips</i>

Atomic absorption spectroscopy (AAS)

The information on lead analysis using flame AAS shows that lead can only be measured down to 0.05 ppm = 50 ppb. The calibration curve in the diagram shows measurements of lead in ppb therefore the more sensitive GFAAS method must have been used.

Chemists who use AAS

The laboratory analysers need to be confident that the sampling techniques are providing suitable samples. For example, dissolved oxygen levels can be affected by how far from the water/air interface a sample is collected, temperature of water at time of collection, exposure of sample to light after collection if it contains any photosynthetic organisms and contact with any oxidisable carbon compounds. The analysers may issue instructions on how samples are collected and they need to check that these instructions have been carried out.

Understanding a chemistry job description

- 1 Essential criteria for this position include:
 - PhD in relevant area
 - experience in organic synthesis
 - ability to work as part of a team
 - good oral and written communication skills.
- 2 Two criteria which are not essential but would be desirable include:
 - some experience in molecular modelling and molecular design
 - some experience in HPLC.
- 3 Two criteria which indicate the importance of collaboration
 - ability to work as part of a team
 - good oral and written communication skills.
- 4 Criteria involving collaboration are essential.

Trace elements and AAS

- 1 $1 \text{ hectare} = 100 \text{ m} \times 100 \text{ m} = 10\,000 \text{ m}^2$
 $100 \text{ g / hectare} = 100 \text{ g} / 10\,000 \text{ m}^2 = 0.0100 \text{ g / m}^2$
- 2 $0.0100 \text{ g} / 100 \text{ kg} = 0.0100 \text{ g} / 100\,000 \text{ g} = 0.100 / 1\,000\,000$
 $= 0.100 \text{ ppm by weight}$

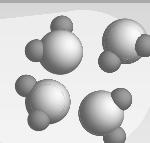
Chemical principles

Stage 6 Chemistry principle	Branch
oxidation of chemical species is due to loss or gain of electrons	<i>electrochemistry</i>
radiation from radioactive elements can be detected by an instrument	<i>environment</i>
concentrations of reactants and products in a mixture at equilibrium will alter so as to counteract any change in concentration, temperature or gas pressure	<i>industrial</i>
the properties of a biopolymer depend on its structure	<i>biomolecular</i>
particles can absorb or emit electromagnetic radiation	<i>analytical</i>

Monitoring and managing modern internal combustion engines

- CO is a poisonous gas. It bonds strongly with the oxygen carrier, haemoglobin, to form very stable carboxyhaemoglobin. O₂ does not bond as strongly when it forms oxyhaemoglobin. Formation of carboxyhaemoglobin reduces the oxygen carrying capacity of the blood. Quite low blood CO concentrations can be fatal.
- Hydrocarbons can react with oxidising gases such as O₂, NO₂ and N₂O to form a range of harmful chemicals including carcinogens (cancer producing substances).
- NO_x react with oxygen in sunlight producing ozone, a toxic reactive gas. NO_x react with water producing some acids in acid rain.

C₈H₁₈ + 25/2 O₂ → 8CO₂ + 9H₂O represents λ = 1 as all the hydrocarbon is changed to CO₂ and H₂O maximising the heat released.

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understand**SYMBOLIC** H_2O formulas
equations
calculations**MICRO**particles
energy
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Exercises – Part 2

Exercises 2.1 to 2.2

Name: _____

Exercise 2.1: Chemists in your area

- 1 List the variety of chemical occupations in your area. If you cannot find any in the immediate area then either extend the area you are investigating or choose chemists reported on in the media eg. Australian Government Analytical Laboratory (AGAL) chemists who analysed all drug samples for the 2000 Sydney Olympics.

- 2 Name the industry or enterprises employing the chemists.

- 3 Identify the branches of chemistry in which the chemists work. Use the thirteen divisions of the RACI to describe the branches.

- 4 Choose one of the chemists and describe their work in more detail.
Also explain a chemical principle that the chemist uses in their work.

Exercise 2.2 : Using data from AAS measurements to evaluate the effectiveness of pollution control

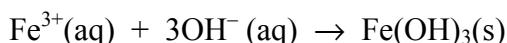
Arsenic rich ground water is a serious threat to 20 million people in Bangladesh. Solar oxidation and removal of arsenic (SORAS) is a simple method that uses irradiation of water with sunlight in PET plastic or other UV transparent bottles to reduce arsenic levels in drinking water.

Ground water in Bangladesh contains Fe^{2+} ions and Fe^{3+} ions. Fe^{3+} forms an insoluble hydroxide precipitate.

Arsenic with an oxidation state of three, As(III), is only weakly adsorbed but arsenic with an oxidation state of five, As(V), is strongly adsorbed to the surface of iron(III) hydroxide particles as they precipitate out of solution.

The SORAS method involves adding six drops of lemon juice to each litre of water in a 1.5 L PET plastic bottle 80% filled with water. The bottle is shaken vigorously for 30 seconds then placed horizontally in sunlight for 4 to 5 hours.

The UV energy, oxygen and water in the bottle produce oxidising conditions.



At the end of the day the bottle is left to stand vertically. The As^{5+} is adsorbed onto the surface of the brown Fe(OH)_3 as it precipitates overnight.

The next morning the liquid is decanted or filtered through fine cloth leaving the last 100 mL containing iron(III) hydroxide and arsenic(V) to be discarded.

The citric acid from the lemon juice enhances the photochemical oxidation of the arsenic(III) and leads to much faster formation and settling out of precipitate.

Here are some AAS measurements of total As from an investigation into this method.

Sample / total arsenic concentration	Absorbance
ground water before SORAS treatment	0.28
ground water after SORAS treatment	0.13
0.050 ppm	0.12
0.100 ppm	0.23
0.150 ppm	0.35

- 1 Draw a calibration curve of absorbance vs total arsenic concentration.

- 2 Use your curve to determine the total arsenic concentration in ground water before and after SORAS treatment.
-
-

- 3 Evaluate the effectiveness of this method if the recommended daily intake of arsenic by an adult is set at 150 µg.
-
-
-
-

- 4 Many Australian laboratories are replacing AAS equipment which analyses one element at a time with much more expensive equipment which allows analysis of up to 60 different elements at once.

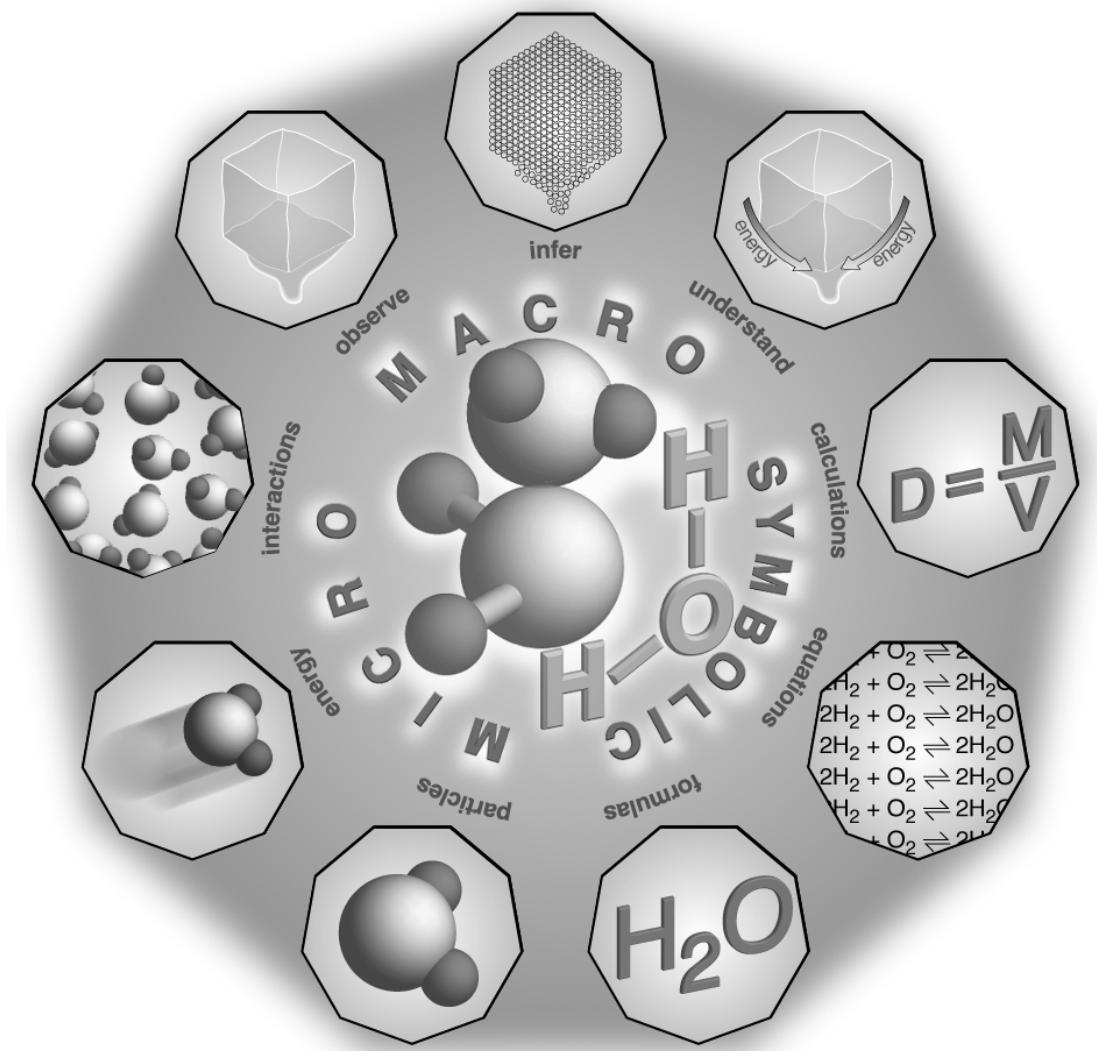
a) Why can this expense be justified?

b) Suggest a use for superseded AAS equipment.

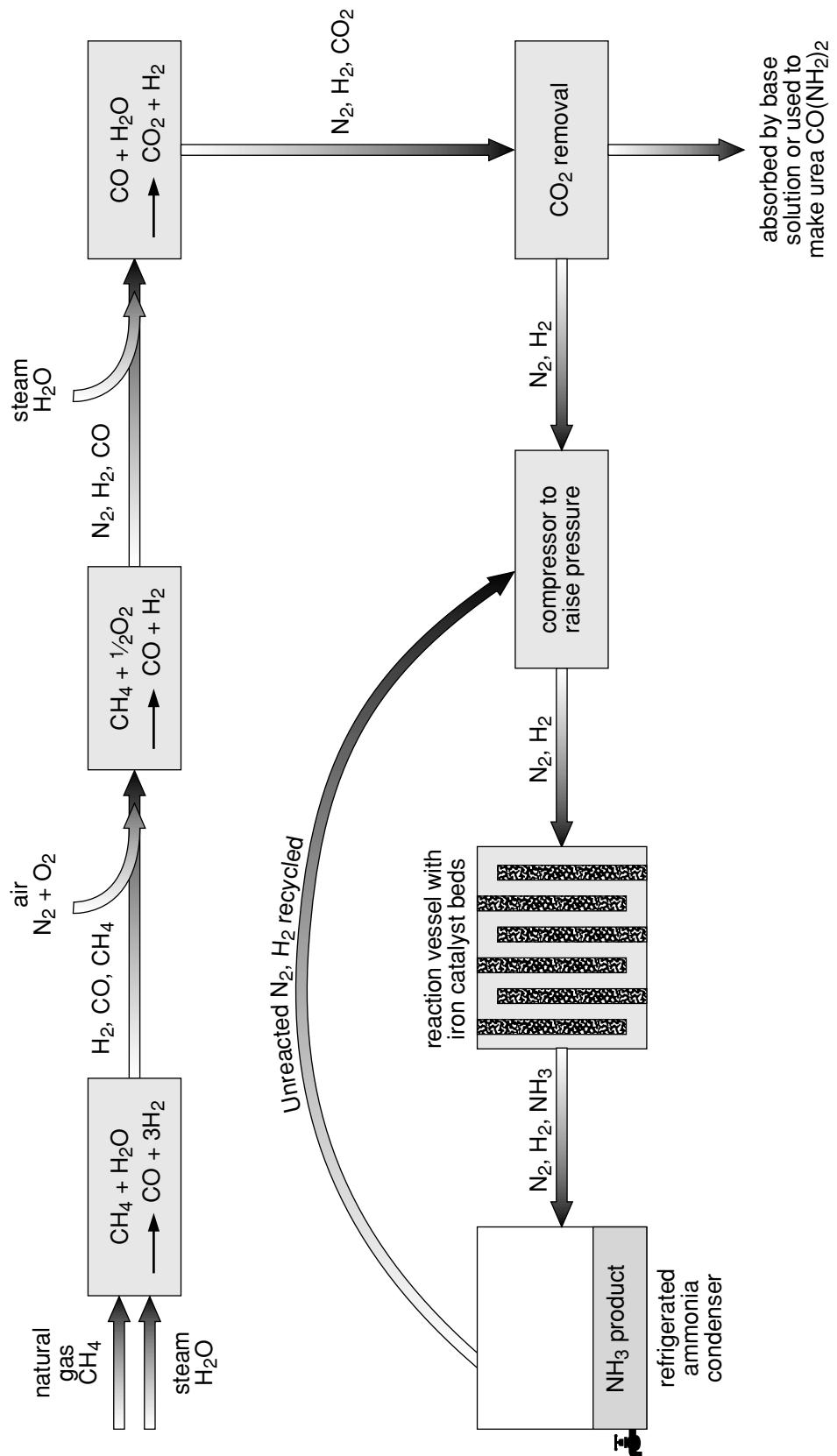


Chemical monitoring and management

Part 3: Haber-Bosch process



Flow chart of the Haber-Bosch process.



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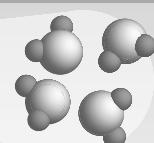
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H_2O formulas
equations
calculations



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energy
interactions



Contents

Introduction	2
Fritz Haber	4
Nitrogen fixation in nature.....	5
The Haber-Bosch process.....	7
Properties and uses of ammonia.....	7
The reaction.....	8
Appendix: Fritz Haber.....	15
Suggested answers.....	19
Exercises – Part 3	21

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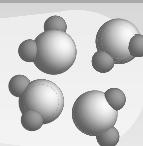
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equations
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Introduction

Chemical processes in industry require monitoring and management to maximise production and ensure quality control. In this part you will study one of the most famous chemical processes of all – the Haber-Bosch process for making ammonia from nitrogen and hydrogen.

In 1898 scientists were warning of the world's first resource crisis. A lack of nitrogen fertilisers could lead to mass starvation. In 1900 two-thirds of the world's nitrogen fertiliser came from salt deposits in Chile and guano deposited by sea birds on islands off Peru. By 1913 Germany was importing one third of the nitrate exported from South America.

Scientists were trying to find ways of changing the N_2 in air to nitrates or ammonia for use as nitrogen fertilisers. The German Fritz Haber (pronounced *Frits Harber*) succeeded in developing a high pressure, high temperature catalysed method of reacting nitrogen and hydrogen to form ammonia NH_3 .

Haber received the Nobel Prize for chemistry in 1918 for this work while Carl Bosch (pronounced *Karl Bosh*) was awarded a half share in the 1931 prize for his pioneering work on high pressure chemical engineering. This is the only chemical process ever for which two Nobel Prizes have been awarded – in 1918 for the chemistry and in 1931 for the chemical engineering.

The Haber-Bosch process has not been superseded and today over 100 million tonnes of ammonia are made each year in hundreds of Haber-Bosch plants. The cost of nitrogen fertiliser is the most important economic factor in determining the production of food throughout the world.

Practically all the hydrogen used in producing ammonia by the Haber-Bosch process comes from hydrocarbons in fossil fuels. One litre of crude oil (or its natural gas equivalent) is used to make one kilogram of ammonia which is used to produce twelve kilograms of grain (typically 5-10% nitrogen-rich protein). Limited fossil fuel resources have major implications for the world's food supply!

In Part 3 you will be given opportunities to learn to:

- identify and describe the industrial uses of ammonia
- identify that ammonia can be synthesised from its component gases, nitrogen and hydrogen
- describe that synthesis of ammonia occurs as a reversible reaction that will reach equilibrium
- identify the reaction of hydrogen with nitrogen as exothermic
- explain why the rate of reaction is increased by higher temperatures
- explain why the yield of product in the Haber process is reduced at higher temperatures using Le Chatelier's principle
- explain why the Haber process is based on a delicate balancing act involving reaction energy, reaction rate and equilibrium
- explain that the use of a catalyst will lower the reaction temperature required and identify the catalyst(s) used in the Haber process
- analyse the impact of increased pressure on the system involved in the Haber process
- explain why monitoring of the reaction vessel used in the Haber process is crucial and discuss the monitoring required.

In Part 3 you will be given opportunities to:

- gather and process information from secondary sources to describe the conditions under which Haber developed the industrial synthesis of ammonia and evaluate its significance at that time in world history
- gather and process information from secondary sources to perform calculations to demonstrate the effect of volume, temperature and concentration changes on product formation in the Haber process.

Extracts from *Chemistry Stage 6 Syllabus* © Board of Studies NSW, originally issued 1999. The most up-to-date version can be found on the Board's web site at http://www.boardofstudies.nsw.edu.au/syllabus99/syllabus2000_list.html

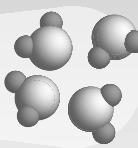
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calculations



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Fritz Haber

The story of Fritz Haber and the process he developed to make ammonia from atmospheric nitrogen illustrates the impact of an application of chemistry on society and the impact of change in society on the chemist.

Read through the information in the *Appendix*.

Exercise 3.1 requires you to form a team of yourself and one to four other people to analyse the appendix information. Each member of your team will look at the information from a particular aspect so that they can give a brief report on that aspect.

The aspects that your team can investigate include:

- scientific/chemical
- historical
- economic
- social/moral/ethical
- political.

Because you are the chemistry student it is probably best if you cover the scientific/chemical aspect unless you have another team member with greater chemical knowledge than yourself. Try to involve other people that you know have an interest in history or economics or social issues or politics.

Start thinking now about which family members, friends or acquaintances you should approach to help you with this activity. You will need about 30 minutes of their time. They need to read the information and then give you their thoughts on the particular aspect you allocate to them.

Complete Exercise 3.1.



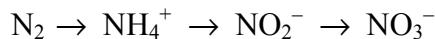
Nitrogen fixation in nature

The nitrogen molecule N₂ is inert. The nitrogen to nitrogen triple bond is the strongest bond that exists between any two identical atoms! The bond energy is 945 kJ/mol. The table below demonstrates how important atmospheric nitrogen N₂ (sometimes called dinitrogen) is as a resource of N in the biosphere.

Nitrogen source	% that is nitrogen (by mass)	Amount in the biosphere (billions of tonnes)
dinitrogen N ₂	100	10 000
ammonia NH ₃	82	10
urea CO(NH ₂) ₂	47	0.01
amino acids	8–27	10
proteins	15	1

Fixation of nitrogen involves the breaking of N to N triple bonds and the formation of bonds between N and other atoms. In nature this occurs in:

- nitrogen-fixing bacteria living in plant roots. They have enzymes containing molybdenum at the active site able to reduce N₂ to NH₄⁺ ions which can be oxidised to NO₂⁻ and NO₃⁻ ions



N oxidation state 0 -3 +3 +5
reduction → oxidation → oxidation

- lightning strikes and high temperature fires where temperatures exceed 1300°C. The energy combines N₂ and O₂ to form NO which is oxidised to NO₂ that reacts with water to form HNO₃ and NO₃⁻.



Give the nitrogen oxidation state for each step and describe each step as oxidation, reduction or no redox.



N oxidation state
ox/red/no redox → → → →

Check your answer.

Like lightning and fires, the Haber process uses an energy intensive approach. So far, no low temperature pathway of industrially producing ammonia has been found. Extensive research using compounds of molybdenum and other transition metals continues.

MACRO

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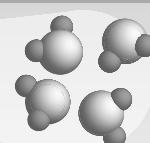
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equations
calculations



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The Haber-Bosch process

Properties and uses of ammonia

Ammonia NH_3

Colourless gas with a **pungent**, suffocating odour.

Highly water soluble.

MP $-78^\circ C$

BP $-33^\circ C$

Easily liquefied under pressure

$NH_3(l)$ density = 0.77 g cm^{-3}

Over 80% of the ammonia produced is used as fertiliser, often injected directly into the soil as liquid. Also used to make the solid fertilisers urea $CO(NH_2)_2$ and ammonium nitrate NH_4NO_3 .

Used to make nitric acid which is raw material for production of explosives such as ammonium nitrate NH_4NO_3 , trinitrotoluene (TNT) and nitroglycerine (dynamite)

Used as a refrigerant, cleaning and bleaching agent and in household cleaners.

Important in the manufacture of plastics such as nylon and acrylonitrile, pharmaceutical chemicals and other carbon compounds.

Ammonia can be used as a convenient source of hydrogen by cracking into nitrogen (safely vented to the atmosphere) and hydrogen.



The hydrogen can be used to hydrogenate fats and oils from unsaturated to saturated and to reduce iron oxides to iron in salvaging shipwrecks.



Identify and describe three industrial uses of ammonia.

Check your answers.



Inspect the labels of cleaning solutions and medicines at home for terms such as ammonia, ammonium, quaternary ammonium, ammonium hydrochloride. List information about the products in the table below.

Term	Product	Product use

The reaction



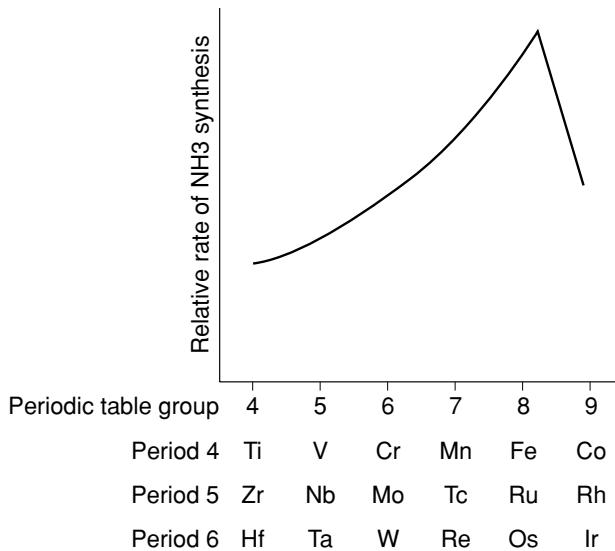
Note that the reaction is reversible and exothermic.

Industrial conditions typically used are:

- temperature 450 – 500°C
- pressure 200 atmospheres
- catalyst.



Use the information in the graph below to identify the periodic table group providing the best catalysts. Evaluate which catalyst is most likely to be used in industry. Give any criteria you used in your evaluation.

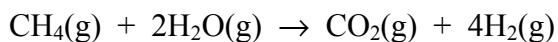


Check your answer.

Raw materials

Raw materials needed for the reaction are:

- nitrogen from the air
- hydrogen, normally obtained by reacting steam with the CH₄ in natural gas.



The acidic gas CO₂ can be either:

- removed by reaction with a base
- diverted to a urea fertiliser manufacturing plant
- liquefied for use in fire extinguishers or soft drinks.

Yield and equilibrium

The yield of a chemical reaction is the amount of desired chemical produced compared with the theoretical maximum amount. Yield is usually expressed as a percentage. In the reaction:



the yield would be 100% if the reaction went to completion. Because this is a reversible reaction the yield of ammonia at equilibrium is always less than 100%.

The yield is only about 20% under typical industrial conditions of:

- temperature 450 – 500°C
- pressure 200 atmospheres
- iron catalyst.

This means only about 20% of the nitrogen and hydrogen changes to ammonia.

Remember Le Chatelier's principle? 'The concentrations of reactants and products in a mixture at equilibrium will alter so as to counteract any change in concentration, gas pressure or temperature'.

Applying this principle you should be able to see three ways to maximise the yield of ammonia:

- 1 Decrease the concentration of ammonia by removing the ammonia product will make the system produce more to re-attain equilibrium.

Use the boiling points of the reactants and products

N_2 –196°C H_2 –253°C NH_3 –33°C

to suggest a way of removing ammonia product from the gas mixture.



Check your answer.

- 2 Increase pressure because 4 moles of reactants produce 2 moles of product equilibrium position shifts towards fewer moles of gas.
- 3 Decrease temperature (remove heat energy) because the reaction is exothermic heat energy can be regarded as a product

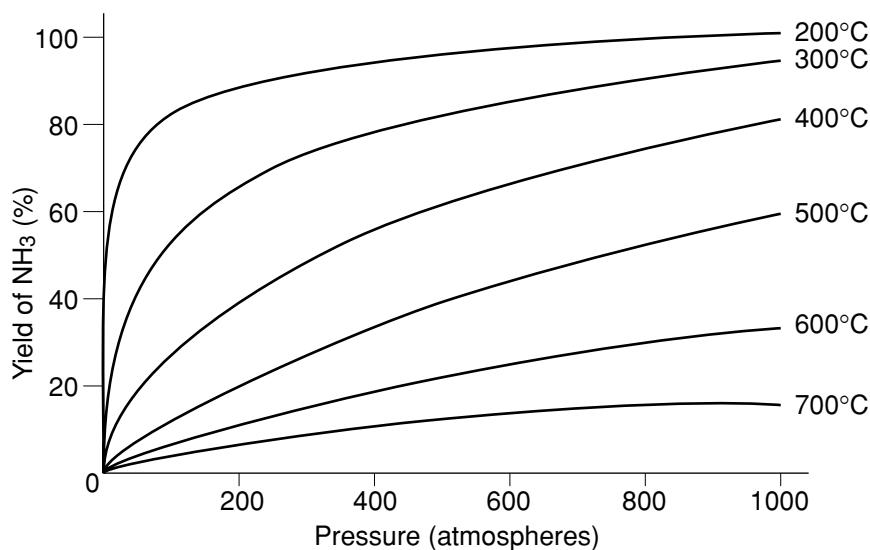


Just as removing ammonia product caused the system to produce more ammonia so removing heat energy (decreasing heat energy) causes the equilibrium position to shift to the right.

Unfortunately, lowering the reaction temperature lowers the rate of reaction.

Yield and rate of reaction

Study this graph that shows how % yield of ammonia depends on temperature and pressure but gives no information on rate of reaction.



Percentage yield of ammonia at different temperatures and pressure.



- 1 The yield is increased by _____ pressure and _____ temperature.
The yield is favoured by _____ temperature but the rate of chemical reaction is favoured by _____ temperature.

It is no good having a 90% yield at a low rate if a 20% yield obtained at a much faster rate produces much more product at the end of the day. A compromise temperature is required that achieves the most economical combination of yield and rate. This is typically 450–500°C.

Other considerations are:

- temperatures which are too high can damage the catalyst
- the higher the pressure the more expensive the containing equipment and its maintenance.

In a country where high pressure equipment has to be imported and is expensive, to maintain a lower pressure may be most economic.

On the other hand, in a country where the engineering industry can build and maintain high pressure equipment the Haber-Bosch process could be carried out at pressures as high as 1000 atmospheres.

- 2 In Australia temperatures of 450-500°C and 150-180 atmospheres pressure are most economical. Use the diagram above to predict typical % yields.
-

Check your answers.

Catalyst action

A catalyst lowers the activation energy required for a reaction. By using a catalyst a lower temperature is required for the reaction to proceed at an appreciable rate.

There are two main types of catalysis (catalyst reactions).

- **Homogeneous catalysis** where the catalyst is the same phase as the reactants eg. catalysis of esterification by H⁺ where the H⁺, alkanic acid and alcohol are all in the liquid phase
 - **Heterogeneous catalysis** where the catalyst is in a different phase (usually solid) while the reactants are all in solution or gaseous phase.
- 1 Assess whether the Haber-Bosch process is homogeneous or heterogeneous catalysis. Justify your answer.
-
-



The Haber-Bosch process catalyst consists of iron crystals in a fused mixture of other oxides. Sulfur, phosphorus and arsenic poison the catalyst by bonding strongly and permanently causing changes to the surface.

Gases such as oxygen, water vapour and carbon oxides are temporarily adsorbed poisons that reduce the amount of catalyst surface available. If the catalyst surface is kept free of poisons, nitrogen and hydrogen are adsorbed onto the catalyst surface and the atoms rearrange into ammonia molecules which then leave the catalyst surface.

The catalyst may last from several months to several years depending on the temperature used and exposure to poisons.

- 2 Explain why poison monitoring should be carried out before the catalyst reaction vessel is reached while temperature monitoring is most important in the catalyst reaction vessel.

- 3 After the gas mixture leaves the reaction vessel it is cooled to only -25°C to liquefy the ammonia. The unreacted nitrogen and hydrogen gases are recycled through the reaction vessel. What reaction condition enables ammonia with a liquefaction temperature/boiling point of -33°C to be liquefied at -25°C ?

Check your answers.

Simulating the ammonia synthesis reaction



What you will need

- small container such as a matchbox or for takeaway food
- small lollies/seeds to represent hydrogen such as cachous (silver balls)/hundreds and thousands or mustard seeds/peppercorns
- larger lollies/seeds to represent nitrogen such as Jila® mints or frozen peas
- a sticky substance to represent the catalyst surface such as jam/honey/vegemite®/peanut butter/mustard.

What you will do

- 1 Coat one of the inside surfaces of the box with the sticky substance. This represents the catalyst surface onto which hydrogen and nitrogen must be adsorbed before they can react.
- 2 Insert three small lollies/seeds and one large lollies/seeds into the box and shake gently until you cannot hear or feel particles bouncing around. If the particles do not stop moving you may need to use a coating that is stickier to represent the catalyst. Alternatives to food spreads are hand creams and toothpaste.

- 
- 3 When the particles have stuck open up the container slowly and draw the positions of the 'hydrogen' and 'nitrogen' particles adsorbed on the catalyst surface.
 - 4 Leaving these particles already stuck on the catalyst surface insert six small lollies/seeds and two large lollies/seeds. This represents double the original pressure. Shake until most cannot be seen, heard or felt bouncing around.
 - 5 Open the box and draw the positions of the hydrogen and nitrogen particles adsorbed on the catalyst surface.

What you must not do: eat anything used in a matchbox.

Discussion

- 1 Have any of the first lot of particles moved from their original positions? _____
When N₂ and H₂ molecules are adsorbed onto the iron catalyst the bonds between the atoms are often broken and N and H atoms can move slowly over the catalyst surface.
- 2 When you increased the pressure of particles hitting the catalyst surface did you get more particles adsorbed onto the surface? _____
Are more or fewer N and H atoms now in positions where they could join to form NH₃ molecules? _____
- 3 The reaction is exothermic. This favours nitrogen and hydrogen atoms reacting to form ammonia rather than ammonia reacting to form nitrogen and hydrogen molecules.
If you are not sure why draw a diagram of energy versus reaction pathway for the ammonia synthesis reaction. Compare the activation energy for the synthesis of ammonia with the activation energy for the decomposition of ammonia.



Complete Exercises 3.2 to 3.4.

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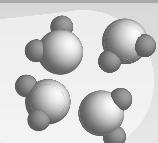
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Appendix: Fritz Haber

In the nineteenth century it was realised that the addition of chemicals as fertilisers could have a major impact on agricultural crop yields. The addition of nitrogen as nitrate or ammonium salts, phosphorus in phosphate salts and potassium in potassium salts were particularly effective in increasing yields.

By the end of the nineteenth century, scientists were warning that a lack of nitrogen fertilisers could lead to mass starvation. Scientists were trying to find ways of changing the nitrogen in air to compounds such as nitrates or ammonia for use as nitrogen fertilisers.

At the beginning of the twentieth century Germany was importing large amounts of nitrate salts from guano deposits in Chile and islands off the coast of Peru. The deposits in Chile were 350 km long and 1.5 m thick! Guano deposits are built up from droppings of seabirds rich in phosphates and nitrogen compounds.

The seabirds eat fish from the surrounding ocean. The remains of the fish skeletons provided the phosphates while breakdown products from the muscles (flesh) of the fish provided nitrogen compounds.

By 1913 Germany was importing one third of the nitrate exported from South America. When World War 1 broke out in 1914 the British navy prevented the import of nitrogen compounds into Germany. Without nitrogen compounds Germany would run out of explosives and food. Fritz Haber, a chemist, developed the method of synthesising ammonia in the laboratory.

Carl Bosch overcame the high pressure engineering problems and supervised the building of ammonia industrial plants during the war period. The Haber-Bosch process enabled Germany to become independent of imported nitrogen compounds.

Fritz Haber was born into a Jewish family living in Prussia in 1868. His father was a prosperous chemical merchant dealing mostly in dyes.

In 1904 some Austrian industrialists asked Haber to study the formation of ammonia from nitrogen and hydrogen. A year later he published a book on gas reactions.

In this book Haber recorded the production of small amounts of ammonia from nitrogen and hydrogen at 1000°C using an iron catalyst. He developed bench top equipment made of metals that operated at up to 200 atmosphere pressure and 600°C. No previous industrial chemical process had used such high pressures. His prediction of 8% yields created interest amongst industrialists. A full scale plant was producing 6 500 tonnes per year in 1913.

During the 1914-1918 war Haber was a patriotic German who accepted and followed the state's decrees. Initially, he worked on developing better antifreezes for the war against Russia. Haber is better known for development of chemical warfare as he organised the first large scale release of chlorine gas which killed thousands of Allied troops and even hundreds of German troops.

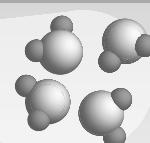
By 1918, 200 000 tonnes of ammonia was produced in Germany each year. A process developed to increase agricultural crop yields and prevent starvation may have doubled the length of the First World War from 1914 to 1918. Possibly the end of the war came sooner because the military had diverted ammonia production from food crops to nitric acid production for explosives.

Haber regarded gas warfare as no more barbaric than other means of warfare. However his wife disagreed and wanted Haber not to work in gas warfare. This disagreement was partly responsible for the despair that led his wife to suicide in 1915. The awarding of the 1918 Nobel prize in chemistry to Haber was controversial. His role in chemical warfare initially left Haber isolated from scientific communities outside Germany. His expertise was recognised when he served on the League of Nations Committee on Chemical Warfare.

At the end of the war the Allies demanded 50 000 tonnes of gold from Germany. Haber attempted to reduce this burden by trialling processes to extract gold from sea water. Unfortunately the concentration of gold was too low to extract economically. The true concentration of less than 8 µg per tonne was about a thousand times below what Haber had thought existed.

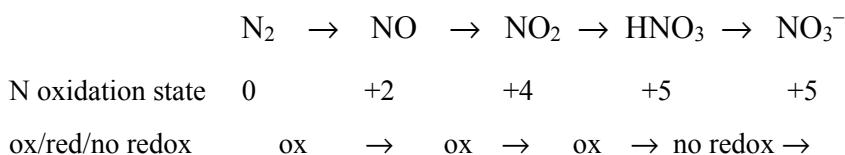
As well as the synthesis of ammonia, Haber made important contributions in electrochemistry. He devised a glass electrode for measuring pH and studying fuel cells. Although he failed to recover gold from sea water economically his work laid the foundations for the extraction of bromine from the oceans.

Haber's life as a scientist ended when Hitler came to power in 1933. The Nazi race laws forced his Jewish staff to resign. Haber also resigned writing '... for more than forty years I have selected my collaborators on the basis of their intelligence and their character and not on the basis of their grandmothers'. Haber died in 1934 of heart disease in Switzerland while on his way to take up a position as head of physical chemistry at an institute in Palestine.

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Suggested answers

Nitrogen fixation in nature



Properties and uses of ammonia

- making solid fertilisers
- making nitric acid to make explosives
- refrigerant liquid
- cleaning agent
- bleaching agent
- convenient and safe source of hydrogen

The reaction

Periodic table group 4 elements produce the fastest rate of reaction. Iron is the most common and cheapest of these and so most likely to be used.

Yield and equilibrium

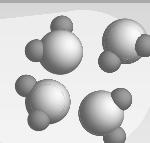
Cooling/refrigeration would condense the ammonia product out as a liquid leaving unreacted nitrogen and hydrogen to be recycled.

Yield and rate of reaction

- 1 The yield is increased by *high* pressure and *low* temperature.
The yield is favoured by *low* temperature but the rate of chemical reaction is favoured by *high* temperature.
- 2 About 20% yield for most economical Australian conditions.

Catalyst action

- 1 The Haber-Bosch process is heterogeneous catalysis because gaseous reactants react on a solid catalyst surface.
- 2 Poison monitoring is carried out before the reaction vessel to stop the permanent poisons S, P and As and the temporary poisons O₂, H₂O, CO and CO₂ from reaching the catalyst. Temperature monitoring is most important in the reaction vessel because the reaction is exothermic, higher temperatures reduce yield and high temperatures can damage the catalyst.
- 3 Ammonia liquefies at –33°C at normal atmospheric pressure. Because the pressure is many times atmospheric pressure the ammonia molecules are closer together, forces of attraction are more effective and the ammonia gas liquefies at a higher temperature. The higher temperature of –25°C is sufficient to liquefy ammonia, but not nitrogen or hydrogen, at these high pressures.

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Exercises – Part 3

Exercises 3.1 to 3.4

Name: _____

Exercise 3.1: Evaluating the significance in world history of Haber's industrial synthesis of ammonia

Briefly describe the person who reported on:

- scientific/chemical
- historical
- economic
- social/moral/ethical
- political aspects.

Briefly outline the main points made about the following aspects of ammonia synthesis.

- scientific/chemical

- historical

- economic

- social/moral/ethical

- political.
-
-

- 1 By 1900 improvements in water quality and safe disposal of sewage had led to rapid increases in Europe's population. Outline why there was so much interest in 'fixing' atmospheric nitrogen – that is reacting the most common gas in the air with other elements to form nitrogen compounds?
-
-
-
-

- 2 Complete the table to identify the two most important scientific/engineering contributions to the development of the Haber-Bosch process

Year	Scientist/engineer	Brief outline of the contribution

- 3 Discuss why the award of the 1918 Nobel Prize in chemistry to Haber 'for the synthesis of ammonia from its elements' was controversial.
-
-
-

- 4 Account for the Haber process being called the Haber-Bosch process.
-
-
-
-

- 5 Evaluate the significance in world history of Haber's industrial synthesis of ammonia.

Exercise 3.2: Using Le Chatelier's principle

Use Le Chatelier's principle to explain why the yield of product in the Haber process is reduced at higher temperatures.

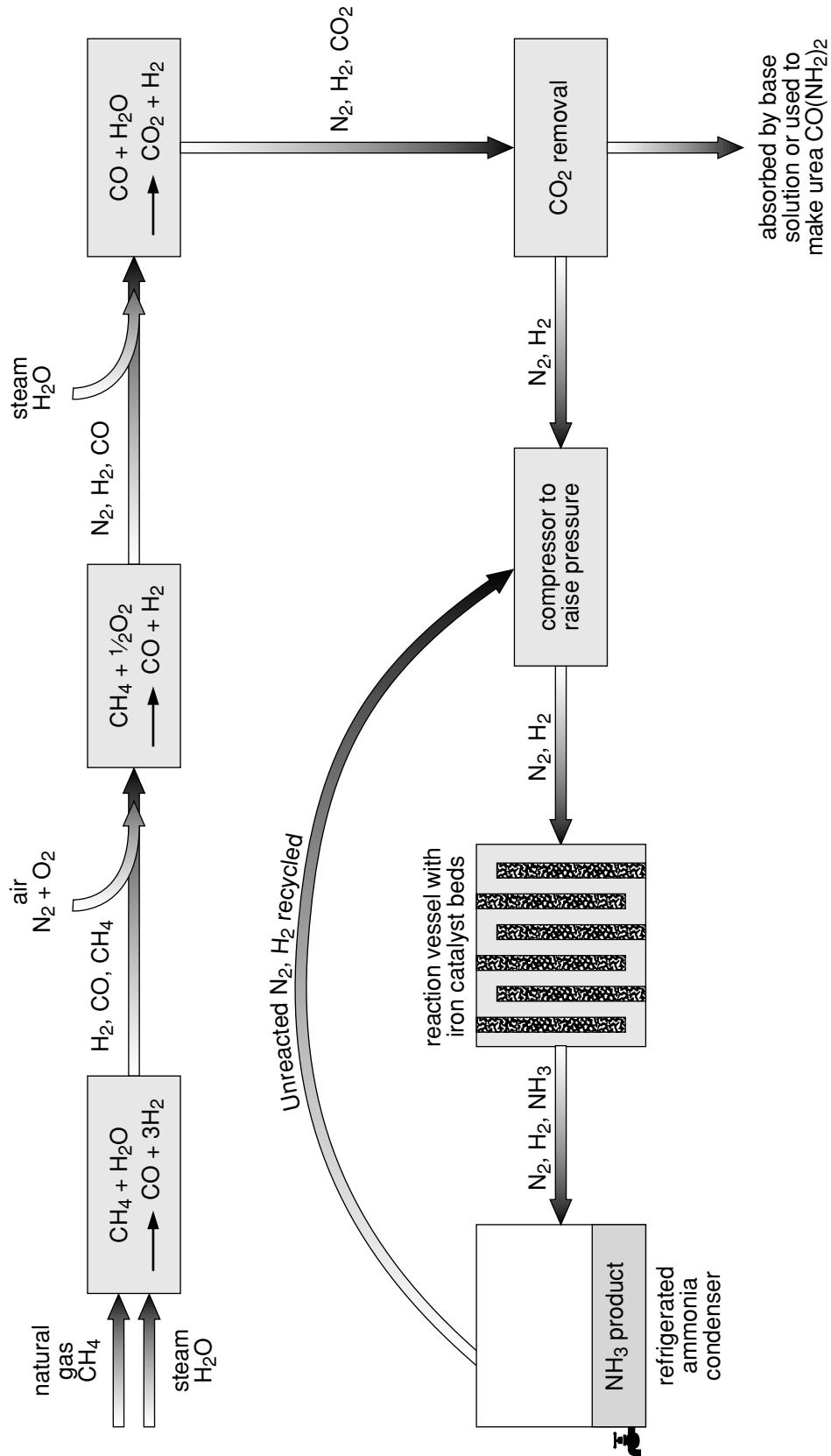
Exercise 3.3: Monitoring the Haber-Bosch process

Using the symbols given in the table below show where you would position monitors in a Haber-Bosch plant to better manage production

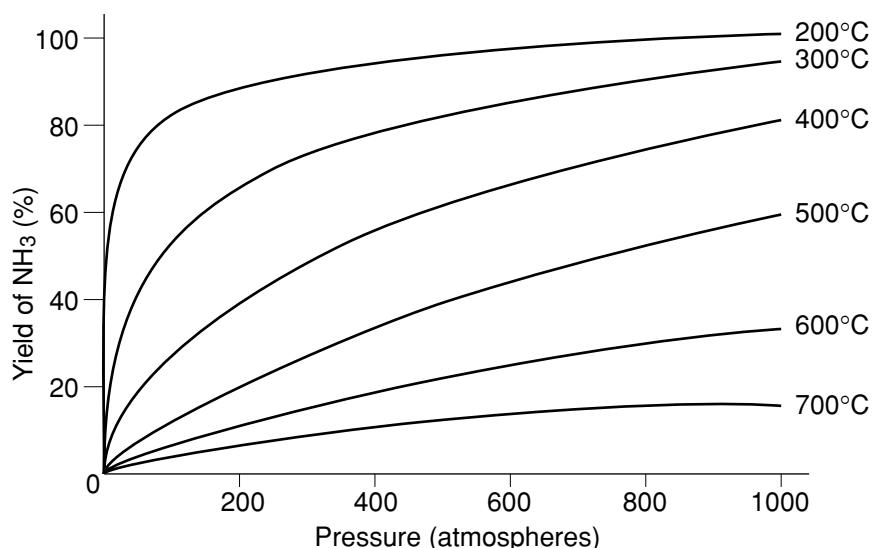
Monitor	Symbol
sulfur	S
phosphorus	P
arsenic	As
temperature	T
temperature	T
temperature	T
pressure	PR
oxygen	O
carbon oxides	Cox
water	H ₂ O

- 1 Mark these symbols at appropriate places on the diagram on the next page.
- 2 Explain why monitoring of the reaction vessel is crucial.

Flow chart of the Haber-Bosch process



Exercise 3.4: Effect of volume, temperature and pressure (concentration) changes on product formation in the Haber process



- 1 Volume decrease (compression) and pressure increase both result in an increase in concentration of particles in a gas phase reaction. Predict the effect of an increase in concentration of particles on the Haber process equilibrium.

- 2 A mixture of 34 kg of nitrogen and hydrogen (in the mole ratio one N₂ : three H₂) is subjected to 500 atmospheres of pressure and 400°C temperature.
- a) Use the graph to predict what % conversion to ammonia occurs.

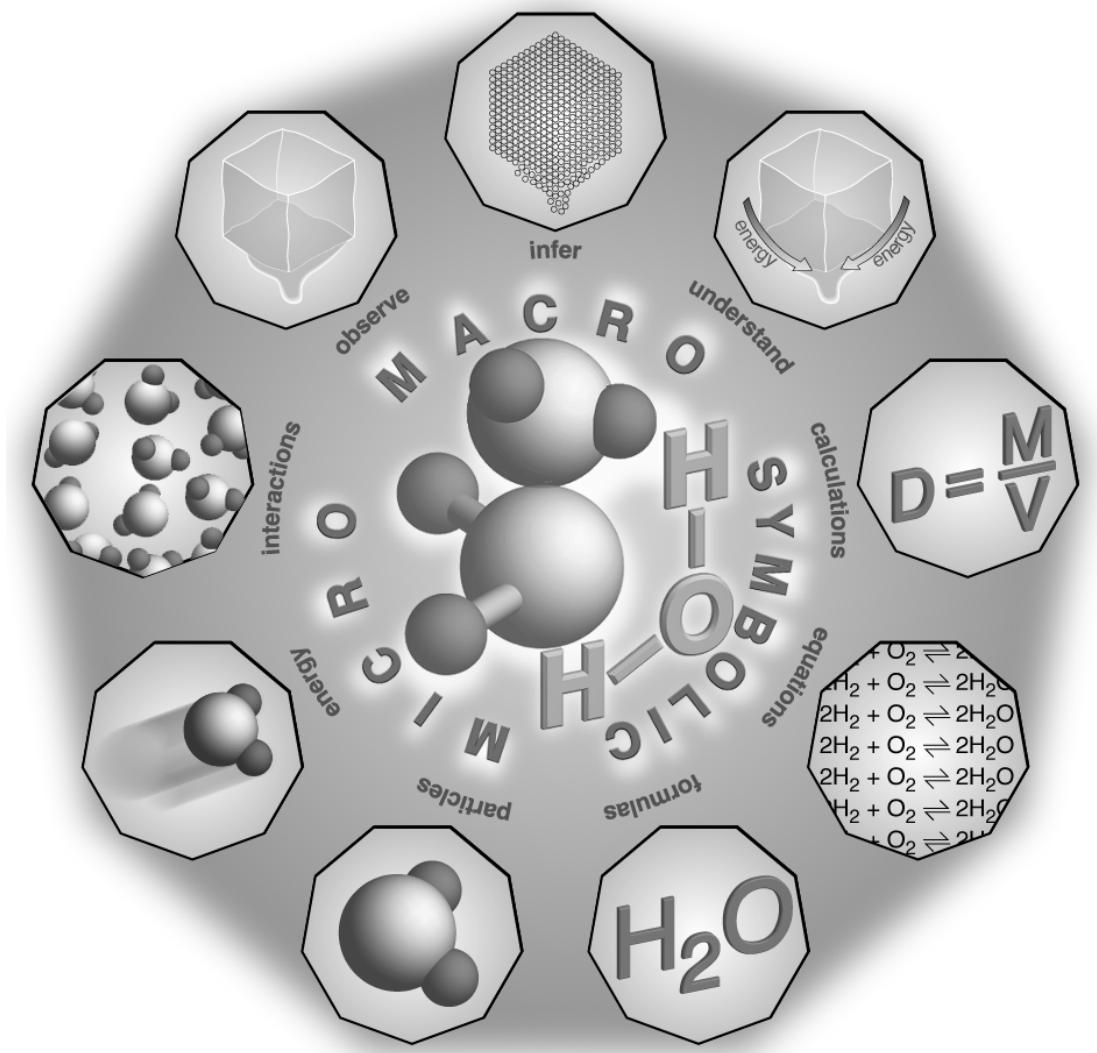
- b) Calculate the amount of ammonia produced under these conditions.

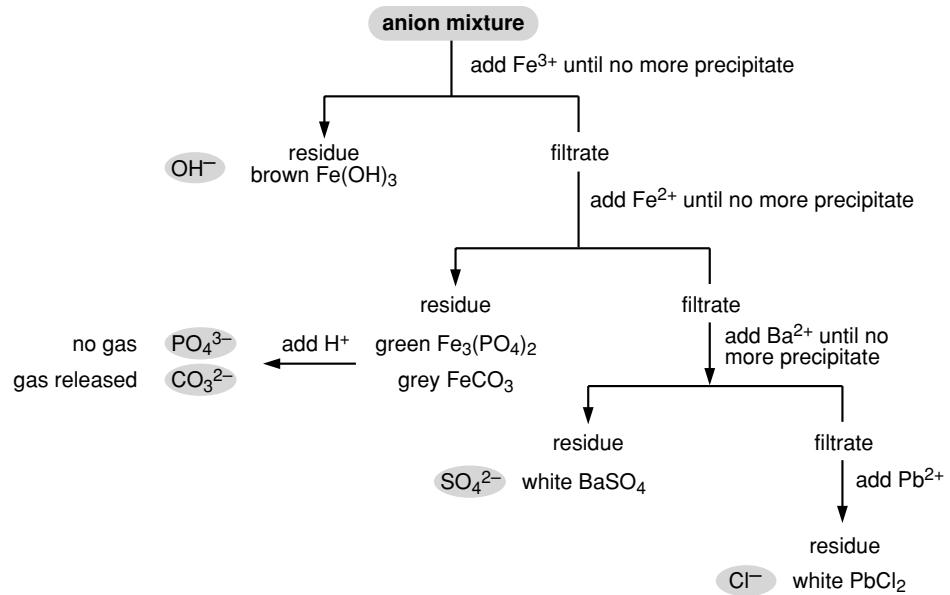
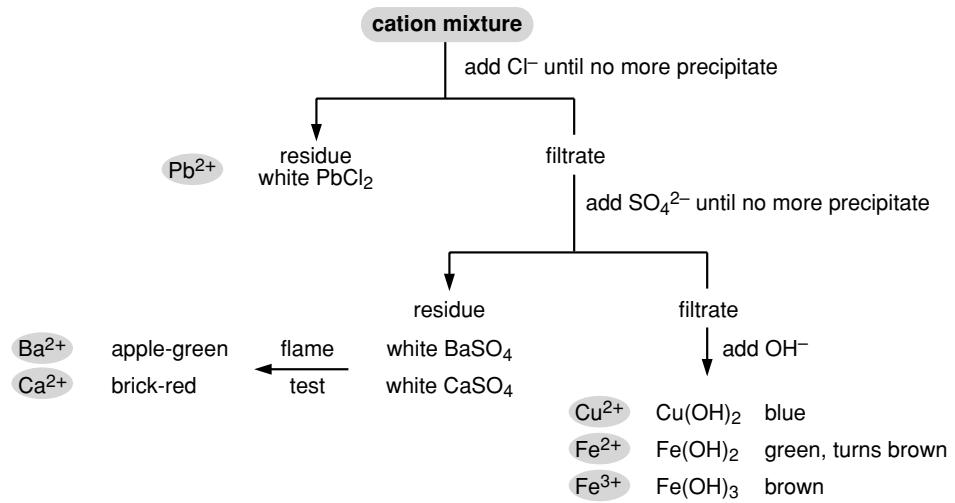
- c) Calculate the mole ratio N₂ : H₂ : NH₃ under these conditions.

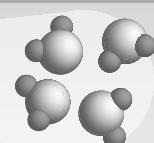


Chemical monitoring and management

Part 4: Chemical analysis





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Contents

Introduction	2
Qualitative analysis – identifying ions.....	4
Using ions to test for oppositely charged ions	6
Using flame tests to distinguish certain metals.....	7
Qualitative analysis of mixtures	8
Quantitative analysis of manufactured products.....	11
Phosphorus content in detergent	11
Nitrogen content in fertiliser	13
Sulfate content of fertiliser	16
Ethanol in wine or beer	18
Citric acid in orange juice.....	19
Water, alcohol and aspirin content of a medicine.....	21
Suggested answers.....	23
Exercises – Part 4	25

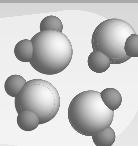
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Introduction

A wide range of manufactured products, including food, drugs and household chemicals are analysed by chemists to control quality. Products are analysed to determine their chemical composition and/or energy content.

The information supplied with these products is based on quality control and scientific investigations that ensure impurities are not at unacceptable levels. This gives you opportunities to make health-related choices and decisions that can affect your personal well-being. By contrast illegally manufactured products, such as illegal drugs, are of uncertain quality and purity. This lack of quality control can have unforeseen and unknown health effects, both short term and long term.

This part gives you opportunities to learn about the qualitative analysis of certain ions and the quantitative analysis of a number of common manufactured products.

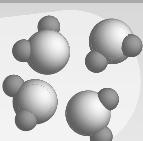
In Part 4, you will be given opportunities to learn to:

- describe chemical tests to identify the following:
 - anions:
 - phosphate
 - sulfate
 - carbonate
 - chloride
 - cations:
 - barium
 - calcium
 - lead
 - copper
 - iron
- deduce the ions present in a sample from the results of these tests.

In Part 4 you will be given opportunities to:

- perform first-hand investigations to carry out a range of tests, including flame tests, or use information from secondary sources to identify the following ions:
 - phosphate
 - sulfate
 - carbonate
 - chloride
 - barium
 - calcium
 - lead
 - copper
 - iron
- gather, process and present information to describe and explain evidence for the need to monitor levels of one of the above ions
- identify data, plan, select equipment and perform first-hand investigations to analyse the:
 - phosphorus content in detergent
 - nitrogen content of fertiliser
 - sulfate content of lawn food or fertiliser
 - ethanol in wine or beer
 - citric acid in orange juiceand explain the chemistry involved in each case
- analyse information to evaluate the reliability of the results of one of the above investigations and to propose solutions to problems encountered in the procedure
- solve problems by devising a procedure that could be used to identify the water content, alcohol content and aspirin content of a medicine.

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Qualitative analysis – identifying ions

ions		PO_4^{3-}	SO_4^{2-}	CO_3^{2-}	Cl^-	OH^-
	colour	all these anions are colourless				
Ba^{2+}	colourless	w, insol	w, insol	w, insol	w, sol	w, sol
Ca^{2+}	colourless	w, insol	w, insol	w, insol	w, sol	w, sl sol
Pb^{2+}	colourless	w, insol	w, insol	w, insol	w, sl sol	w, insol
Cu^{2+}	blue	bl, insol	bl, sol	g, insol	g, sol	bl, insol
Fe^{2+}	pale green	g, insol	g, sol	grey,insol	g, sol	g, insol
Fe^{3+}	yellow	pink, sl sol	y, sol	*	bn, sol	bn, insol

LEGEND: sol = soluble sl sol = slightly soluble insol = insoluble
w = white bl = blue g = green y = yellow bn = brown

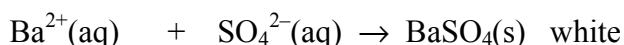
* brown precipitate formed is iron(III) hydroxide, not iron(III) carbonate

Solubility of some salts.



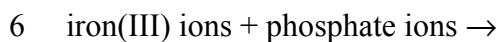
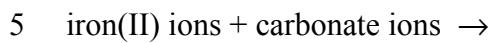
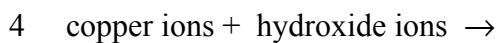
Using the information in the solubility table above write balanced ionic equations for the following reactions. Include the colour of any precipitate formed. The first question is answered for you.

1 barium ions + sulfate ions →



2 calcium ions + carbonate ions →

3 lead ions + chloride ions →



Check your answers.



The unfilled spaces in the table below are where the combination of ions should form a precipitate. Using coloured pencils, shade the spaces with the colour of the precipitate.

ions		PO_4^{3-}	SO_4^{2-}	CO_3^{2-}	Cl^-	OH^-
	colour	all these anions are colourless				
Ba^{2+}	colourless				w, sol	w, sol
Ca^{2+}	colourless				w, sol	
Pb^{2+}	colourless					
Cu^{2+}	blue		bl, sol		g, sol	
Fe^{2+}	pale green		g, sol		g, sol	
Fe^{3+}	yellow		y, sol	*	bn, sol	



Complete the solubility generalisations below.

- 1 Most phosphates are (soluble/insoluble).
- 2 Most carbonates are (soluble/insoluble).
- 3 Most chlorides are (soluble/insoluble).
- 4 Most lead salts are (soluble/insoluble).

Check your answers

You may remember from preliminary modules that nitrates and acetates are soluble. If you want to prepare a solution of a cation look for its nitrate or acetate salt. Similarly sodium, potassium and ammonium salts are soluble so if you want to prepare a solution of an anion look for its sodium, potassium or ammonium salt.

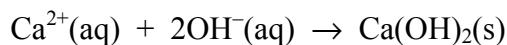
Using ions to test for oppositely charged ions

A convenient way of testing for the presence of an ion in a solution is to add a solution containing an ion of opposite charge that forms a precipitate.

For example, to distinguish between a barium salt solution and a calcium salt solution add a solution containing hydroxide ions eg. NaOH(aq) or KOH(aq).

If no precipitate forms the solution is probably the barium salt as barium hydroxide is soluble (4.7 g of Ba(OH)₂/100 mL water).

If a precipitate forms, the solution is probably the calcium salt as calcium hydroxide is only slightly soluble (0.12 g of Ca(OH)₂/100 mL water):



- 1 Which ion would you use to distinguish between a Ca²⁺ solution and a Pb²⁺ solution? Justify your choice using an equation.

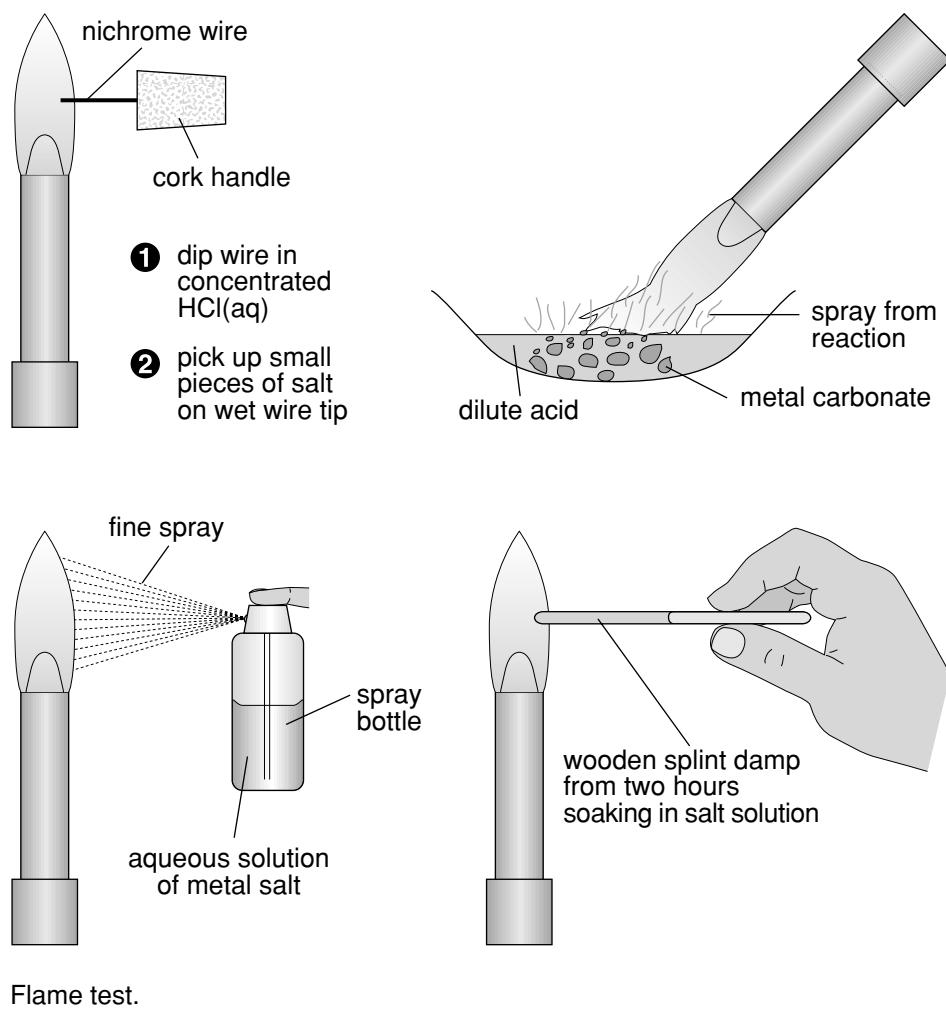
- 2 Which ion would you use to distinguish between a sulfate solution and a carbonate solution? Justify your choice using an equation.

- 3 Which of the six cations in the table would form a white precipitate on addition of sodium carbonate but no precipitate on addition of sodium hydroxide? Justify your choice using an equation.

Check your answers.

Using flame tests to distinguish metals

Some metals emit characteristic colours when their atoms or ions are excited in a flame. The chemical reactions of barium and calcium and their compounds are similar, but barium produces an apple-green colour flame while calcium produces a brick-red colour. Copper metal or compounds produce a flame blue-green colour. The colours are emitted when electrons promoted by heat energy to higher energy levels (further away from the nucleus) in atoms or ions drop back to lower energy levels.

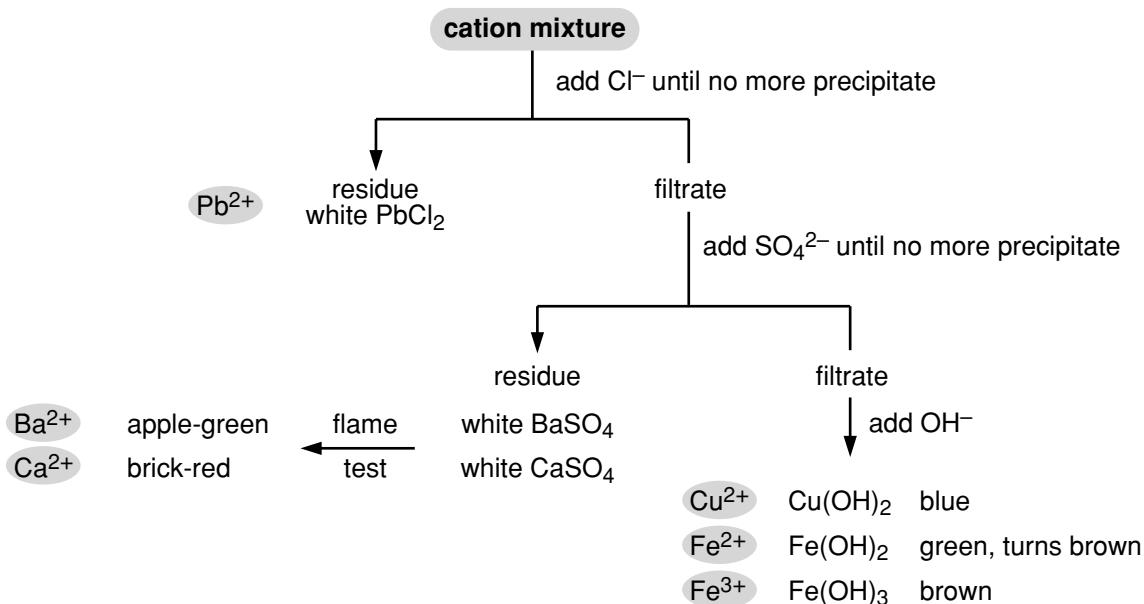


Qualitative analysis of mixtures

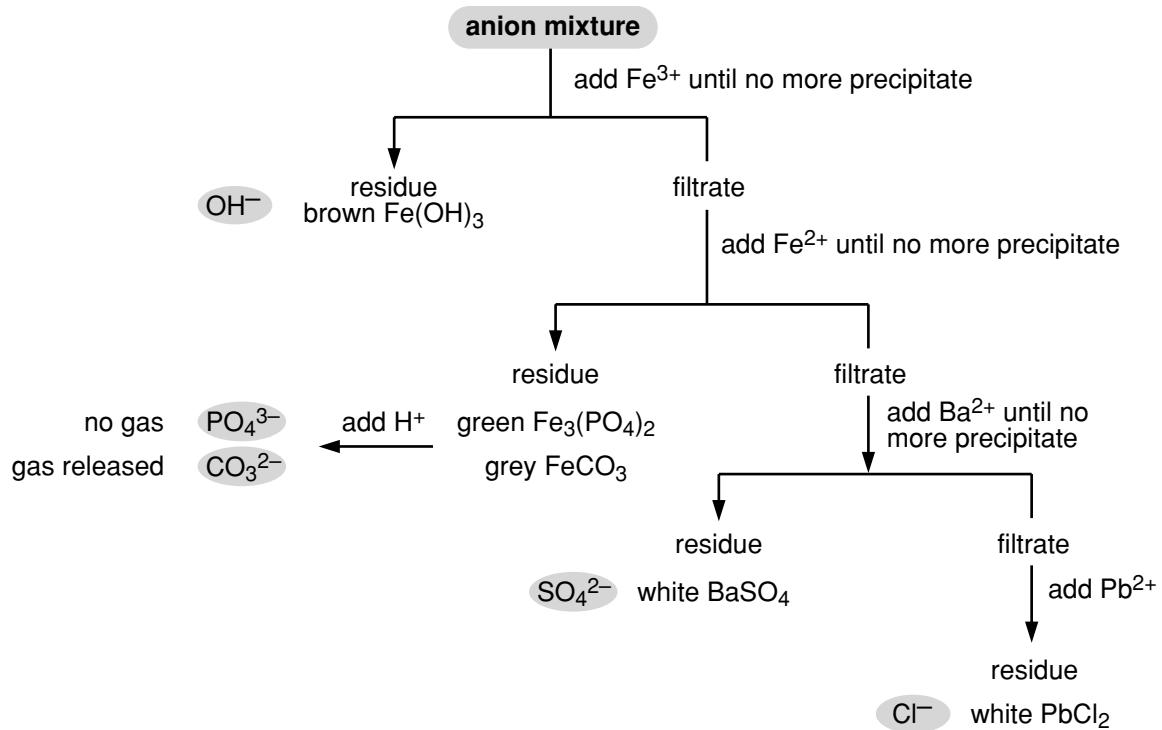
A mixture containing ions must contain positive and negative ions so that the mixture is electrically neutral. As the number of different sorts of ions in a mixture increases the analysis becomes more difficult.

Thought needs to go into ways of separating and testing for one ion at a time. For example, if you carried out a flame test on a mixture of barium and calcium compounds you would not get a distinctive apple green or distinctive brick-red colour. The analysis of a mixture of salts usually involves precipitating an ion from a mixture then testing the filtrate for other ions.

The diagrams below illustrate possible analysis schemes for the cations and anions covered in your course.



Pathways in the analysis of cations.



Pathways in the analysis of anions.



Cation and anion analysis of a solution of two salts gave the results shown below. Use the results to deduce the names of the salts.

1 Salt 1

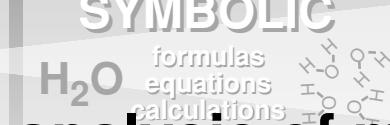
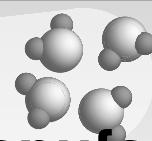
Anion solution added	Cl^-	SO_4^{2-}	OH^-
Observation	-	-	blue precipitate

Cation solution added	Fe^{3+}	Fe^{2+}	Ba^{2+}
Observation	-	-	white precipitate

2 Salt 2

Anion solution added	Cl^-	SO_4^{2-}	OH^-	
Observation	-	-	green precipitate	
Cation solution added	Fe^{3+}	Fe^{2+}	Ba^{2+}	Pb^{2+}
Observation	-	-	-	white precipitate

Check your answers.

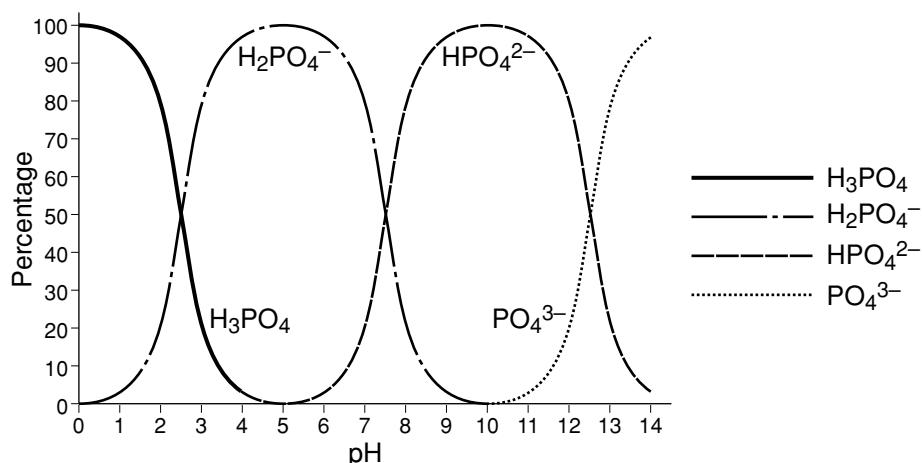
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Quantitative analysis of manufactured products

Phosphorus content in detergent

Nitrogen (as nitrates) and phosphorus (as phosphates) both contribute to eutrophication, but phosphate appears to be the main culprit. Phosphorus compounds in the environment are in three main categories – phosphates, polyphosphates and organic phosphorus compounds.

Phosphates (also called orthophosphates) are present mostly as PO_4^{3-} in very alkaline solution, mostly as HPO_4^{2-} at pH 9 and mostly as $H_2PO_4^-$ at pH 5.

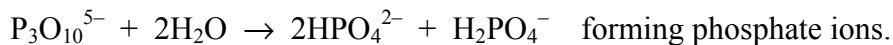


At what pH are phosphate ions in solution 50% HPO_4^{2-} and 50% $H_2PO_4^-$



Check your answer.

Polyphosphates such as sodium tripolyphosphate $Na_5P_3O_{10}$ are present in laundry detergents. The tripolyphosphate ion hydrolyses



Organic phosphorus compounds from body wastes and food residues are found in sewage.

Packets of laundry detergent can be labelled with P to indicate that the product complies with the agreed phosphorus standard if the phosphate level is kept below 7.8 g per wash.

The activity following shows you how to measure the phosphate in laundry detergent gravimetrically. Once the phosphate level is measured the phosphorus level can be calculated.



What you will need:

- a laundry detergent with a stated level of phosphate
- 3 beakers or containers (at least 150 mL, 300 mL, 500 mL)
- filter paper and funnel or coffee filter paper
- Epsom salt $MgSO_4 \cdot 7H_2O$ from a supermarket or pharmacy
- ammonia solution from a supermarket or hardware (at least 2.5% ammonia)
- a long handled spoon or stirrer
- a means of drying wet precipitate such as paper towels and an electric hotplate
- a means of weighing to at least the nearest gram
- a means of measuring about 50 mL volume of liquid.



Laundry detergents contain alkaline substances. Ammonia solution emits a basic gas so work in a well ventilated area. Keep alkaline and basic substances away from your eyes.

What you will do:

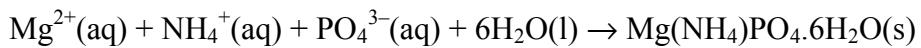
- 1 Accurately weigh out about 10 g of laundry detergent into the 300 mL beaker and dissolve in 100 mL of water _____
- 2 Accurately weigh out about 15 g of Epsom salt into the 150 mL beaker and dissolve in 100 mL of water _____
- 3 Add the contents of the smaller container to the contents of the larger container
- 4 Add 50 mL of ammonia solution and stir the mixture well
- 5 Weigh the filter paper _____
- 6 Filter the precipitate of magnesium ammonium phosphate-6-water $Mg(NH_4)PO_4 \cdot 6H_2O$ from the mixture. Wash with cold water.

- 7 Dry the precipitate on paper towels and an electric hotplate at low heat.
- 8 Weigh the dried precipitate and filter paper and calculate the weight of $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ formed _____

Laundry detergent is a mixture of different compounds, mostly salts. $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ is a white crystalline compound. Give the name of the laundry detergent you used and list the constituents listed on the packet.

Comment on the purity of your precipitate.

Calculations



$$\begin{aligned}\frac{\text{P}}{\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}} &= \\ &= \frac{30.97}{(24.31+14.01+[4.032]+30.97+[64.00]+[6 \times 18.016])} = \frac{30.97}{185.4}\end{aligned}$$

$$\text{weight P} = (30.97 / 185.4) \times \text{weight of dry } \text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O} =$$

$$\% \text{ P (w/w)} = (\text{weight P} / \text{weight detergent}) \times 100\% =$$

Nitrogen content in fertiliser

Nitrogen content in fertiliser can:

- increase the nitrate content of drinking water supplies (nitrate levels above 10 ppm can be toxic to babies)
- increase eutrophication by supplying nitrogen as ammonium ions and nitrate ions
- acidify water supplies through run-off.

If a reaction occurs between solutions rapidly, such as when an acid and a base react, analysis by direct titration is suitable. When a reaction is slow or requires heating or involves a solid a **back titration** is more suitable.

In a back titration a known volume of excess reactant is added and the mixture either stood for a long period or heated to ensure complete reaction; the amount of unreacted reactant is then determined by titration.

You can determine the nitrogen content of ammonium sulfate fertiliser by adding excess NaOH, heating to remove ammonia, then titrating unreacted NaOH against standardised acid.

Analysing the nitrogen content of ammonium sulfate fertiliser



What you will need:

- titration equipment (burette, pipette, conical flask or small syringe, large syringe, medicine measure)
- Quantities listed below are for burette, pipette and conical flask; if you use syringes and a medicine measure use one-tenth the quantities listed but you will need to be able to weigh the ammonium sulfate to 0.01 g.
- a means of weighing ammonium sulfate to at least 0.1 g
 - 1.0 g ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$
 - heat resistant container such as a beaker of at least 300 mL capacity (to hold ammonium sulfate, NaOH solution and acid solution)
 - 200 mL of 0.1 M NaOH solution such as used in Part 4 of the previous module *The acidic environment*
 - acid solution of known concentration such as the diluted vinegar used in Part 4 of the previous module *The acidic environment*
 - phenolphthalein or fresh red cabbage solution indicator
 - means of heating the container such as an electric hotplate.



Protect your eyes against the alkaline NaOH(aq). Basic ammonia fumes are emitted when the mixture of fertiliser and NaOH(aq) is heated. Use a well ventilated area.

What you will do:

- 1 Accurately weigh out about 1 g of ammonium sulfate fertiliser into the heat resistant container _____
- 2 Add the 200 mL of NaOH solution and swirl gently to dissolve the fertiliser
- 3 When the fertiliser is dissolved heat the mixture to gently boiling in a well-ventilated area. You should notice ammonia fumes released.

- 4 Cool the mixture to room temperature, add indicator and titrate with the diluted vinegar of known concentration _____
- 5 Complete the calculations below.

Calculations and results:

- 1 Calculate the moles of acetic acid that reacted in the titration.

- 2 Equation for reaction between CH₃COOH and unreacted NaOH.

3 mol acetic acid = mol unreacted NaOH =

4 mol NaOH which reacted with ammonium ions = mol reacted NaOH
= mol NaOH initially – mol unreacted NaOH
= – =



mol ammonium ions = mol hydroxide ions = mol reacted NaOH

=

- 6 Each ammonium ion contains one nitrogen atom thus

mol ammonium ions = mol nitrogen atoms =

mass of nitrogen = mol nitrogen atoms x 14 g/mol = g

- 7 Nitrogen content of fertiliser = mass of nitrogen/mass of fertiliser

=

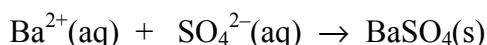
8 % N in (NH₄)₂SO₄ = x 100/1 % =

Compare this figure with the % N figure on a container of ammonium sulfate fertiliser.

Sulfate content of fertiliser

Sulfate ions are an important source of sulfur needed by plants to make certain amino acids.

Sulfate ions can be precipitated with barium ions forming very insoluble barium sulfate. The barium sulfate can be washed, dried and weighed.



The following activity requires access to soluble barium salt and is best carried out in a laboratory. Barium is a heavy metal and its salts are moderately toxic if ingested.

If you do not have access to a laboratory you could make the barium acetate solution by dissolving 2.5 g of barium carbonate in warm vinegar. Barium carbonate BaCO_3 can be purchased from some pottery/craft shops as it is used to make blue glazes.

Wash your hands well after using barium salt. Waste barium salt solution can be disposed of into the waste water (sewage) system.

Analysing the sulfate content of ammonium sulfate fertiliser



What you will need:

- about one hour of time, spread over five days, to complete this activity as the precipitate of BaSO_4 needs to be left overnight to separate
- 1.0 g ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$
- a means of weighing to at least 0.1 g
- 10 mL of a 1.0 M barium salt solution (about 2.5 g of barium acetate or barium chloride made up to 10 mL)
- 10 mL measuring cylinder or a long specimen tube that could hold at least 12 mL
- dropper (pasteur pipette and rubber teat works well) long enough to reach almost to the bottom of the measuring cylinder/specimen tube
- filter papers or coffee filter paper from a supermarket
- means of heating filter paper covered with BaSO_4 precipitate such as an electric hotplate.

What you will do:

1 Place 1.0 g of ammonium sulfate in the measuring cylinder/specimen tube; add about 2 mL of water and shake to dissolve.

2 Add 10 mL of 1.0 M barium salt solution to the ammonium sulfate solution. A white precipitate of very fine particles of BaSO_4 forms.

These BaSO_4 particles are too small to separate from the unreacted ions still in solution with filter paper. An analytical laboratory would use special sintered glass filters to trap such fine particles. You will use a different technique.

3 Leave the BaSO_4 particles to precipitate out overnight until the white precipitate occupies less than 10% of the liquid volume. Remove and discard the clear liquid above the precipitate.

4 Add 10 mL of water to the precipitate, shake to mix precipitate and water. This dissolves soluble ions such as ammonium ions and unreacted barium ions.

Once again leave the BaSO_4 particles to precipitate out overnight until the white precipitate occupies less than 10% of the liquid volume. Remove and discard the clear liquid above the precipitate.

5 Repeat Step 4 at least twice more.



Suppose the concentration of unreacted ions in Step 3 was 2 M.

a) What is the concentration of unreacted ions at the end of Step 4?

b) What will be the concentration of unreacted ions at the end of Step 5?

Check your answers.

6 Weigh a coffee filter paper or two ordinary filter papers.

7 Slowly pour the slurry of about 1 mL of barium sulfate particles and water into the coffee filter paper or a cone made up from two ordinary filter papers.

Do this very slowly spreading slurry over all of the papers surface so that liquid soaks into the paper. The small volume of slurry should not pass through the paper.

8 Place the moist coffee filter paper/double filter paper cone on to the warm source of heat. Be careful the heat source does not burn paper.

The water in the paper should evaporate leaving barium sulfate particles on the filter paper.

9 Weigh the barium sulfate on filter paper

and subtract the filter paper weight to find the dry BaSO₄ weight:

10 The waste filter paper and barium sulfate should be wrapped in paper and disposed of in the solid waste (garbage).

Calculations:

$$\frac{\text{SO}_4^-}{\text{BaSO}_4} = \frac{32.07 + 4 \times 16.00}{137.3 + 32.07 + 4 \times 16.00} = \frac{96.07}{234.4}$$

weight sulfate = (96.07/234.4) x weight of dry BaSO₄ =

% sulfate (w/w) = (weight sulfate / weight fertiliser) x 100% =

Ethanol in wine or beer

The main liquid in wine or beer is water. Ethanol is typically 2-6 % (v/v) in Australian beers and 10-13% (v/v) in Australian wines.

Chemical or physical methods can be used to measure ethanol (alcohol) levels in wine or beer.

Ethanol can be estimated chemically by a reduction-oxidation back titration with standard solutions of either acidified dichromate ($\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$) or acidified permanganate ($\text{H}^+/\text{MnO}_4^-$). The excess of $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$ or $\text{H}^+/\text{MnO}_4^-$ can be measured by titration with a standard solution of Fe^{2+} . A problem with this method is that other carbon compounds besides the ethanol can also react with the $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$ or $\text{H}^+/\text{MnO}_4^-$.

Two physical methods of estimating ethanol in a mixture are:

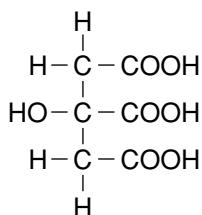
- measuring the density of the mixture and comparing this measurement with density measurements for known mixtures of ethanol and water
- distilling the mixture, collecting and measuring the mass or volume of the fraction that boils off in the range 76°C to 80°C.

All these methods give approximate values because wines and beers can contain over a hundred different chemicals. Some of these can affect the chemical and physical measurements.

Very accurate measurements of ethanol content would require the use of instruments such as in HPLC (high pressure/performance liquid chromatography) or mass spectroscopy (MS).

Citric acid in orange juice

Citric acid HOOC.CH₂.C(OH)(COOH).CH₂.COOH is the main acid found in citrus fruits such as oranges, lemons, limes and grapefruit.



The amount of citric acid can be determined by titration with a standard solution of NaOH using phenolphthalein indicator. As soon as all the acid groups have reacted the juice solution becomes alkaline, the red form of phenolphthalein appears and the juice appears orange. The orange juice is initially yellow but appears orange at the end point!

Because each citric acid molecule has three -COOH acid groups, three moles of NaOH containing three moles of OH⁻ are needed to react with each mole of citric acid.

Analysing citric acid content in orange juice



What you will need:

- a small container of orange juice
 - standardised NaOH solution about 0.1 M
 - phenolphthalein indicator
 - titration equipment (burette, measuring cylinder*, conical flask or small syringe, large syringe, medicine measure)
- (* a pipette is unsuitable here as pulp in the orange juice blocks the jet.)

What you will do:

- 1 Titrate the orange juice with the standardised NaOH using phenolphthalein indicator.
- 2 Calculate the concentration of citric acid in the orange juice.

Calculations:

-  1 25 mL of orange juice required 26.1 mL of 0.0984 M NaOH before the yellow juice containing phenolphthalein turned orange in colour.

Calculate the concentration of citric acid in the orange juice in mol L⁻¹ and in g L⁻¹. Formula weight of citric acid is 192 gmol⁻¹.

- 2 After completing the titration a student noticed that the label of the orange juice listed the ascorbic acid (vitamin C) concentration as 40 mg/L. Ascorbic acid H₂C₆H₆O₆ is a diprotic acid with a formula weight of 176 g / mol. Assess the validity of your calculation of the concentration of citric acid in orange juice by calculating how much of the NaOH would have reacted with ascorbic acid.

Check your answers.

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Water, alcohol and aspirin content of medicine

You are very unlikely to find a medicine that contains aspirin and water. Water reacts with aspirin to form acetic acid and salicylic acid. If aspirin tablets are kept in a sealed container with moisture, the odour of acetic acid (a vinegar smell) could be detected when the container is opened.

Alcohol is often present in medicines because alcohol is a better solvent than water for drugs like aspirin which are molecular rather than ionic compounds.

Methods for qualitatively identifying and quantitatively measuring the content of chemicals in pharmaceutical drugs can be found in pharmacopoeias. A **pharmacopoeia** (pronounced *farm-e-ke-pee-uh*) is a book containing a list of drugs and medicines and describing their preparation, properties and uses. You could ask a pharmacist to show you a copy of a pharmacopoeia.

Water content

Water content can be measured by weighing then drying crushed particles of the medicine at 105°C. Reweighting of the dried medicine enables calculation of the amount of vaporised water and the water content. This method assumes there are no other volatile components in the medicine (such as alcohol) which vaporise on heating.

Another pharmacopoeia method involves adding about one hundred times the medicine volume of toluene. Toluene is a flammable liquid which can be distilled off with the water. After distillation the water layer separates from the toluene and its volume or mass can be measured.

Alcohol content

Alcohol can be distilled off from some mixtures such as Listerine®. Alcohol readily absorbs water so the distillate will most likely be about 96% ethanol and 4% water. Alcohol and water can be separated and measured by distillation with benzene. Benzene is a flammable and toxic liquid banned from use in schools.

Aspirin content

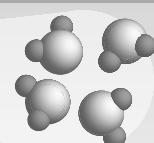
Aspirin content can be measured if there are no other acidic substances by a back titration. A known excess quantity of NaOH(aq) is added and the mixture boiled gently for 10 minutes. The mixture is cooled, phenolphthalein added and unreacted NaOH titrated with acid of known concentration.



Examine the labels on medicines in a pharmacy or a supermarket. Look for water, alcohol and aspirin on the labels. Some may just list the names of the contents (qualitative information) while other labels may give the quantities (quantitative information).



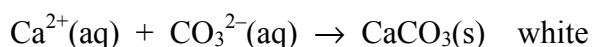
Complete Exercises 4.1 and 4.2.

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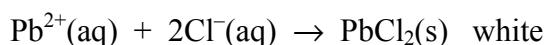
Suggested answers

Qualitative analysis - identifying ions

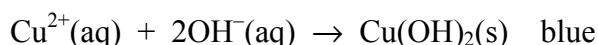
2 calcium ions + carbonate ions →



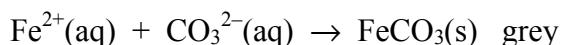
3 lead ions + chloride ions →



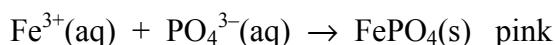
4 copper ions + hydroxide ions →



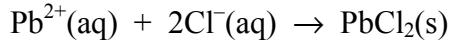
5 iron(II) ions + carbonate ions →



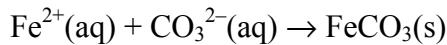
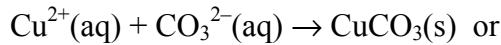
6 iron(III) ions + phosphate ions →

1 Most phosphates are *insoluble*2 Most carbonates are *insoluble*3 Most chlorides are *soluble*4 Most lead salts are *insoluble*.

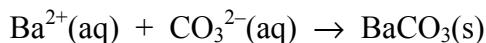
Using ions to test for oppositely charged ions

1 Chloride ion. CaCl_2 is water soluble but PbCl_2 is only slightly soluble and precipitates out if the solutions are concentrated enough

2 Copper ions or iron(II) ions form a soluble sulfate but precipitate with a carbonate solution.



- 3 Barium ions form a white carbonate precipitate



but no precipitate with sodium hydroxide because barium hydroxide is soluble.

Qualitative analysis of mixtures

Salt 1 Cu^{2+} gives a blue precipitate of $\text{Cu}(\text{OH})_2$ with OH^- ; SO_4^{2-} gives a white precipitate of BaSO_4 with Ba^{2+} . Both these precipitates formed thus the salt was CuSO_4 .

Salt 2 Fe^{2+} gives a green precipitate of $\text{Fe}(\text{OH})_2$ with OH^- ; Cl^- gives a white precipitate of PbCl_2 with Pb^{2+} . Both these precipitates formed thus the salt was FeCl_2 .

Quantitative analysis of manufactured products

Phosphorus content in detergent

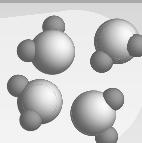
At about pH 7.2–7.4 the mole fraction of HPO_4^{2-} and H_2PO_4^- are both 0.5 corresponding to 50% each.

Sulfate content of fertiliser

- If 1 mL of barium sulfate precipitate in unreacted ion solution has 10 mL of water added the concentration of unreacted ions would drop from 2 M to < 0.2M.
- Two further dilutions would reduce the concentration of unreacted ions to <0.02 M then <0.002 M.

Citric acid in orange juice

- Mol NaOH in titration = $(26.1 \times 10^{-3} \text{ L}) \times (0.0984 \text{ mol L}^{-1}) = 0.00257$ Each citric acid has three COOH groups that can each react with a hydroxide ion thus mol citric acid = $0.00257/3 = 0.000856$
Concentration of citric acid = $0.000856 \text{ mol} / 0.025 \text{ L} = 0.034 \text{ M}$
 $= 0.034 \times 192 \text{ g/L} = 6.6 \text{ g/L}$
- In 25 mL orange juice there is $0.025 \times 40 \text{ mg ascorbic acid} = 1.0 \text{ mg} = 1.0 \times 10^{-3} / 176 \text{ mol} = 0.0000057 \text{ mol}$
Because ascorbic acid is diprotic $2 \times 0.0000057 = 0.000011 \text{ mol}$
NaOH reacts with the ascorbic acid in 25 ml of orange juice. This is only about 1/234 of the moles of NaOH reacting with the citric acid.

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Exercises – Part 4

Exercises 4.1 to 4.2

Name: _____

Exercise 4.1 Evidence for the need to monitor ion levels



Use a search engine to access information from the worldwide web to complete the activity below. Ask your teacher to provide you with downloaded information sources if you cannot access the Internet.

Gather, process and present information to describe and explain evidence for the need to monitor *one* of the following ions:

- phosphate in detergent
 - sulfate in soils near rivers or buried steel pipelines
 - carbonate in cement powder
 - chloride in builder's sand
 - barium in glaze for ceramic kitchenware
 - calcium in human diet
 - lead in drinking water
 - copper in waste water going to a sewage treatment plant
 - iron in water used to wash clothes in laundries.
-
-
-
-
-
-
-
-

Exercise 4.2: Evaluating reliability and proposing solutions to problems

Reliable data is trustworthy data. Evaluating reliability is determining trustworthiness.

- 1 Select one of the investigations that you carried out in quantitative analysis of a manufactured product.

-
- 2 Evaluate the reliability of your results.

- 3 How could you improve the reliability of your results?

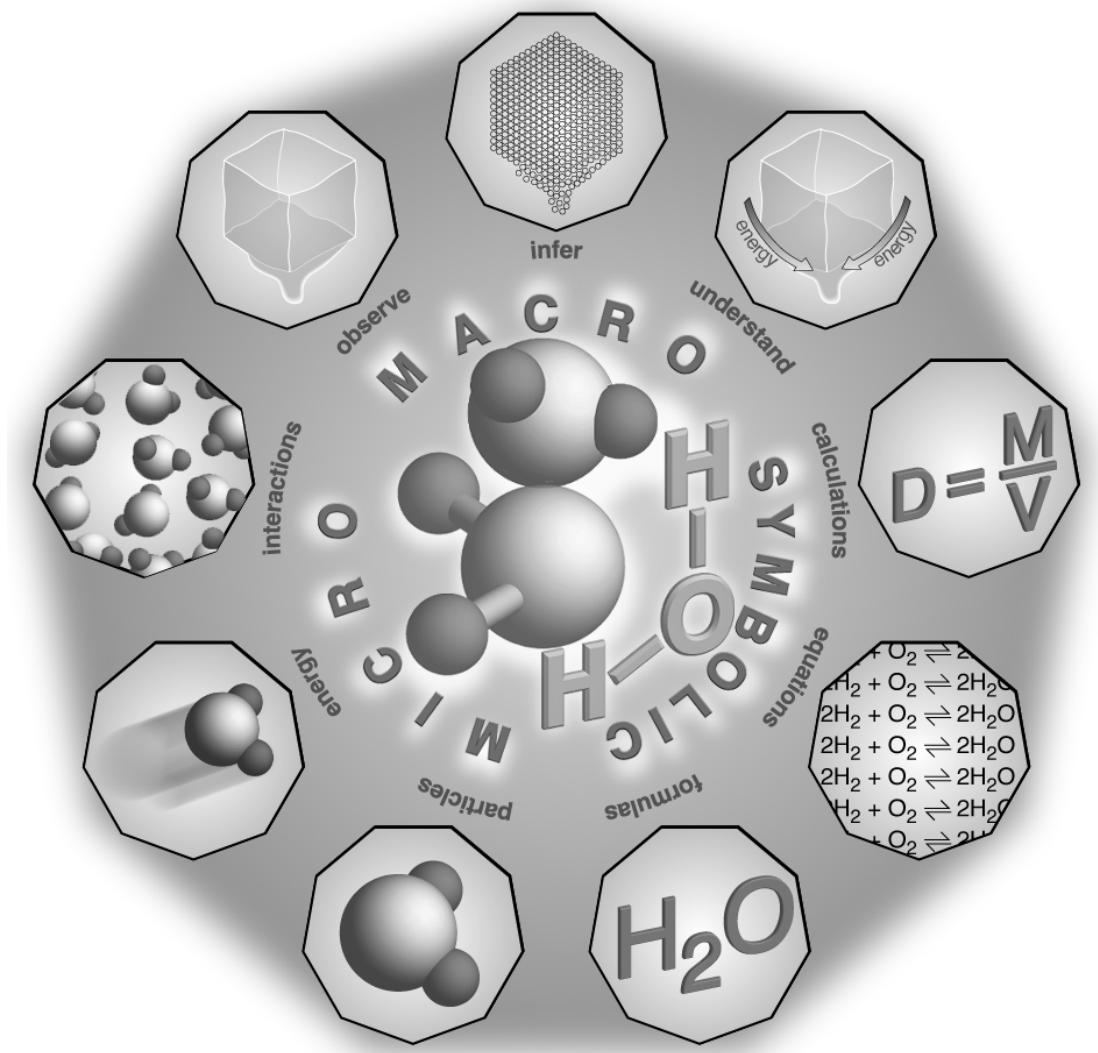
- 4 List problems you encountered in the procedure.

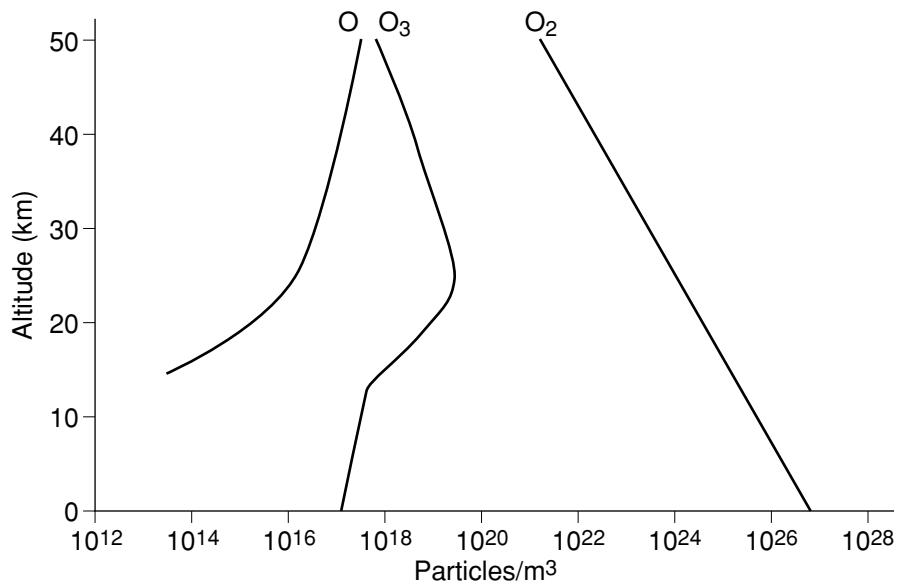
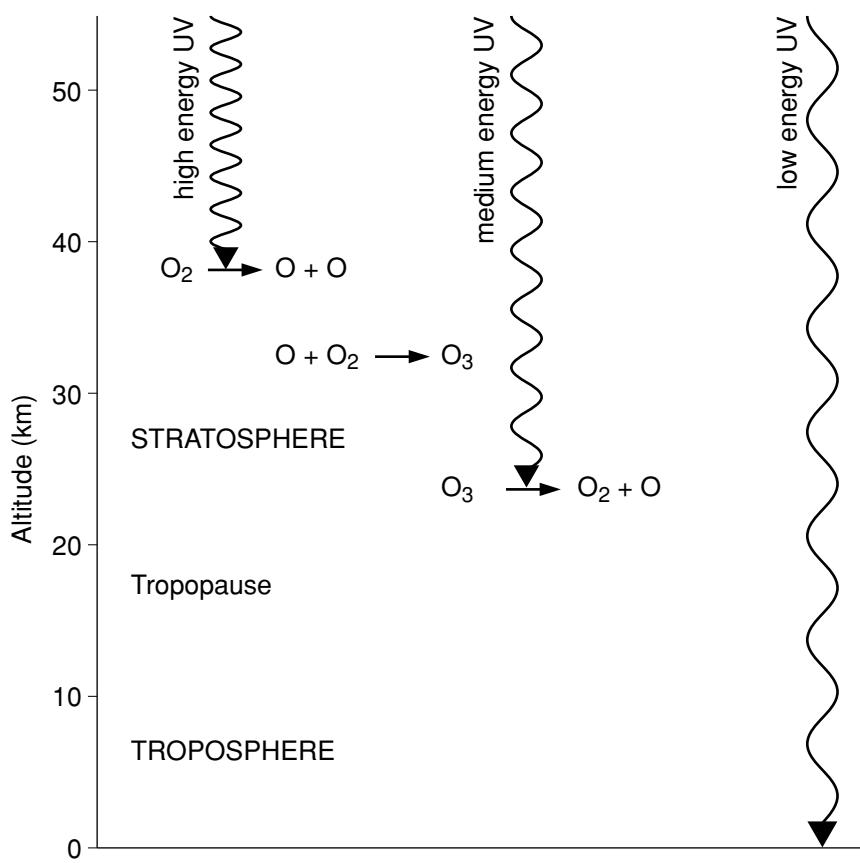
- 5 Propose solutions to these problems.

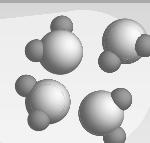


Chemical monitoring and management

Part 5: CFCs and ozone





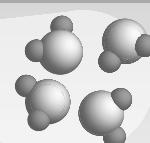
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energy
interactions

Contents

Introduction	3
Structure of the atmosphere.....	5
Good ozone, bad ozone.....	6
Composition of the atmosphere	8
Main air pollutants in the troposphere	10
Ozone formation in the stratosphere	11
Lewis electron dot representations.....	13
Coordinate covalent bonds	13
Comparing the oxygen allotropes O_2 and O_3	15
Comparing O_2 and the oxygen free radical.....	16
Notable scientists	18
Haloalkanes	21
Chlorofluorocarbons.....	21
Haloalkane replacements for CFCs	23
Halons.....	24
Naming straight chain haloalkanes	25
Isomers	26
Measuring atmospheric ozone	27
UV radiation, life and polymers.....	27

Suggested answers 29

Exercises – Part 5..... 33

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understand**SYMBOLIC** H_2O formulas
equations
calculations**MICRO**particles
energy
interactions

Introduction

The chemical composition of the Earth's atmosphere depends on which gases are released and absorbed at the Earth's surface and the rates at which chemical reactions take place in the atmosphere.

Human activity has produced chemicals such as chlorofluorocarbons (CFCs) that have significantly reduced the ozone composition of the upper atmosphere. The less ozone there is in the upper atmosphere the more ultraviolet (UV) radiation reaches the Earth's surface causing more skin cancer, eye damage and harm to plant crops.

The most significant change in the structure of the atmosphere is the formation each spring of an 'ozone hole' over Antarctica. This depletion of the ozone layer is larger in area than Australia and extends towards the southern parts of Australia such as Tasmania.

Chemists monitor changes in ozone concentrations in a number of ways. An international agreement, *The Montreal Protocol on Substances That Deplete the Ozone Layer*, signed in 1987 and since strengthened, is managing the situation by reducing CFC production and use.

Unfortunately, CFCs last for 70-100 years in the atmosphere and it will take many decades before ozone levels return to the safer levels of 40 years ago.

In Part 5, you will be given opportunities to learn to:

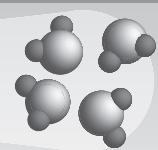
- describe the composition and layered structure of the atmosphere
- identify the main pollutants found in the atmosphere and their sources
- describe ozone as a molecule able to act both as an upper atmosphere UV radiation shield and a lower atmosphere pollutant
- describe the formation of a coordinate covalent bond
- demonstrate the formation of coordinate covalent bonds using Lewis electron dot structures

- compare the properties of the oxygen allotropes O₂ and O₃ and account for them on the basis of molecular structure and bonding
- compare the properties of the gaseous forms of oxygen and the oxygen free radical
- explain the effects of ultraviolet radiation on many polymers including those in living tissue
- identify the origins of chlorofluorocarbons (CFCs) and halogens in the atmosphere
- identify and systematically name straight chain haloalkanes and alkenes with up to eight carbon atoms
- identify and name examples of isomers (excluding geometrical and optical) of haloalkanes up to eight carbon atoms
- discuss the problems associated with the use of CFCs and assess the effectiveness of steps taken to alleviate these problems
- analyse the information available that indicates changes in atmospheric ozone concentrations, describe the changes observed and explain how this information was obtained.

In Part 5, you will be given opportunities to:

- gather, process and present information from secondary sources to compare amounts of components of the atmosphere by moles, mass, by volume and by parts per million
- present information from secondary sources to write the equations to show the reactions involving CFCs and ozone to demonstrate the removal of ozone from the atmosphere
- gather, process and present information from secondary sources including simulations, molecular model kits or pictorial representations to model isomers of haloalkanes
- gather, process and present information from secondary sources such as visual models to identify the effect of UV radiation on biological molecules
- present information from secondary sources to identify alternative chemicals used to replace CFCs and evaluate the effectiveness of their use as a replacement for CFCs.

Extracts from *Chemistry Stage 6 Syllabus* © Board of Studies NSW, originally issued 1999. The most up-to-date version can be found on the Board's web site at http://www.boardofstudies.nsw.edu.au/syllabus99/syllabus2000_list.html

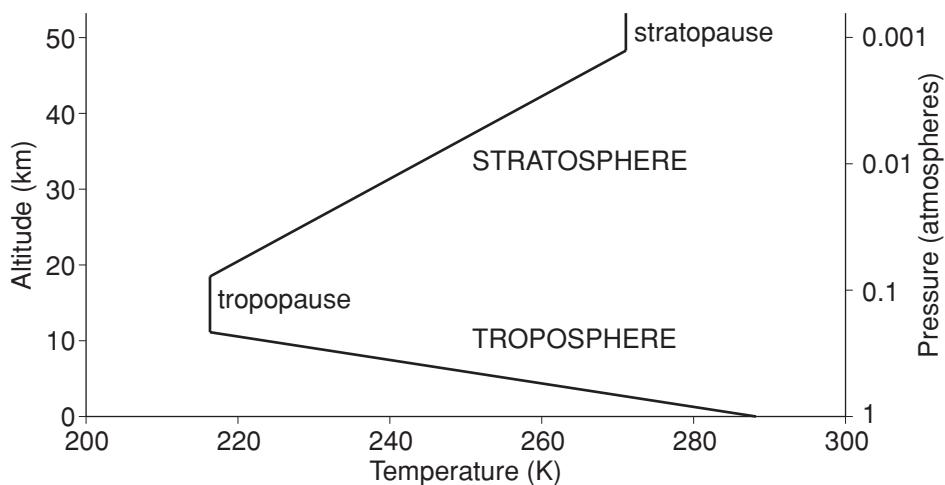
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Structure of the atmosphere

Why does snow appear at the top rather than the bottom of snow covered mountains? If you've ever travelled up a mountain you have probably felt why this is so. The temperature of the layer of air close to the Earth's surface known as the **troposphere**, decreases as you go higher.

Over 90% of the Earth's atmosphere is in the troposphere within 15 km of sea level. The troposphere is where you can see clouds, weather changes and aircraft. Hot air rises from the Earth's surface and considerable vertical and horizontal mixing of gases occurs in the troposphere. From about 9 to 18 km, depending on **latitude**, the air temperature becomes relatively constant in a region called the **tropopause**. This stable troposphere layer reduces movement and mixing of gas molecules.

Above the tropopause is a region from 20 to 50 km above sea level known as the **stratosphere** or upper atmosphere. Less than 1% of the atmosphere's gases are found above 50 km.



Temperature and pressure changes with altitude

The stratosphere contains a layer of ozone gas, O_3 , which absorbs most of the ultraviolet radiation (UV) that can cause harm to life on Earth.

The evolution of this protective ozone layer 600 million years ago enabled plant and animal colonisation of the land surface. The ozone layer of the stratosphere is protection for the existence of life on the Earth's surface. This layer is incredibly thin. If all the ozone in the atmosphere was at the gas pressure you experience at ground level, the layer would be a mere three millimetres thick!

The warmer stratosphere on top of the colder troposphere acts like a lid reducing movement of gas molecules upwards. Warm gas of low density rises upwards through colder gas. Colder gas is trapped under warmer layers of gas because it is of greater density.

Water content of the troposphere varies between 1 and 5% depending on the locality. This water plays a large part in gas movements, temperature changes and precipitations that make up weather in the troposphere.

Condensation and precipitation of water in the troposphere washes water soluble gases such as sulfur oxides and nitrogen oxides out of the air. Hardly any water can pass through the tropopause into the stratosphere. Water concentrations in the stratosphere are four orders of magnitude smaller than in the troposphere – measured in parts per million rather than percentages.

The tropopause also acts as a barrier to the movement of stratospheric ozone down into the troposphere. Ozone in the troposphere originated in the troposphere, not the stratosphere.

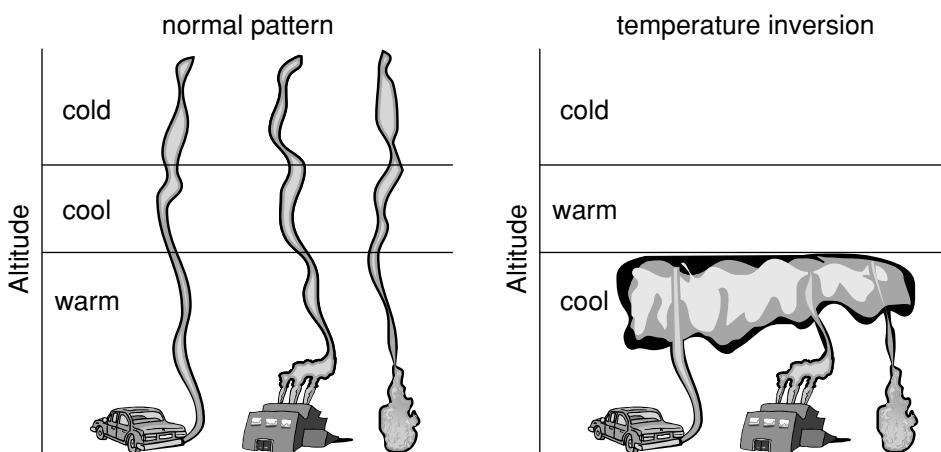
Good ozone, bad ozone

The ozone in the upper atmosphere (stratosphere) is ‘good ozone’. This ozone shield absorbs medium energy UV radiation that is capable of breaking covalent bonds in biological molecules. The ozone concentration in the stratosphere is rarely below 2 ppm reaching a maximum of about 10 ppm at 25 km above sea level.

Ozone in the lower atmosphere (troposphere) is ‘bad ozone’ as it is a pollutant. Ozone (O_3) is a very reactive molecule capable of oxidising many substances. The natural background level of 0.020 ppm is no problem; a level of 0.120 ppm can cause breathing problems for asthmatics; and at 0.200 ppm plant damage becomes obvious.

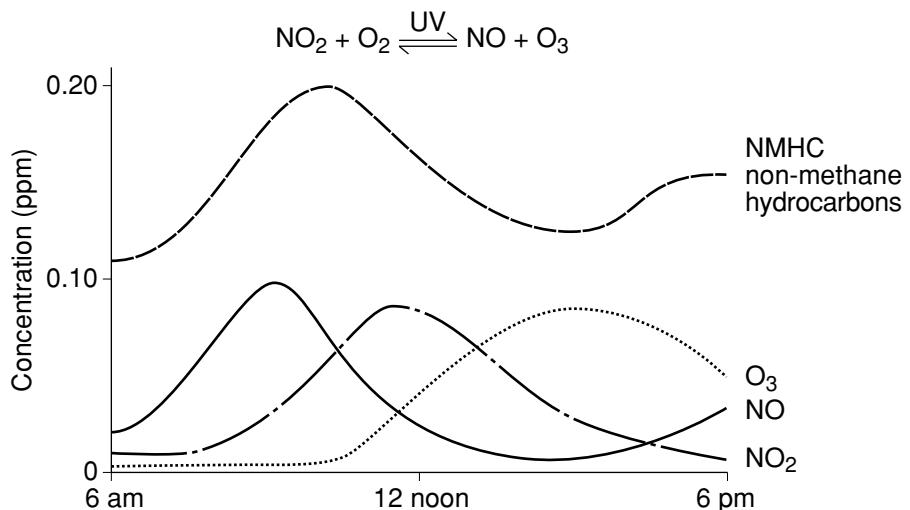
A major source of ozone in the lower atmosphere is photochemical smog. When exhaust and industrial gases such as unburnt hydrocarbons and NO_x collect in still air exposed to sunlight, then reactions occur producing ozone and other chemicals at harmful levels.

Ozone levels are highest in cities when there is no wind and plenty of sunshine just after the morning traffic peak hour. A **temperature inversion** is where a layer of warm air lies above cool air. This traps pollutants and prevents them from rising away from the city. UV causes reactions between the trapped chemicals producing ‘bad ozone’.

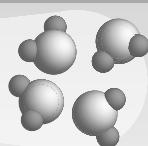


Trapping and concentration of air pollutants by a temperature inversion.

The main NO_x in car exhausts is NO. NO reacts with oxygen in the air to form NO_2 . NO_2 and O_2 can react together when exposed to UV radiation in sunlight forming NO and O_3 . NO and O_3 are both very reactive and can reform the NO_2 and O_2 .



Typical concentrations of photochemical smog reactants in sunlight.
Note: the morning peak hour traffic produces higher concentrations than the afternoon traffic. Note also the sequence of peaks for NO, NO_2 and O_3 .

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Composition of the atmosphere

Component	Molecular formula	ppm by mass
nitrogen	N ₂	755 000
oxygen	O ₂	231 000
argon	Ar	12 800
carbon dioxide	CO ₂	450
NOx	NO, NO ₂	0.002
ozone	O ₃	0.02
sulfur dioxide	SO ₂	0.0002
methane	CH ₄	1
non-methane hydrocarbons	C _n H _{2n+2} for n>1	0.0001
carbon monoxide	CO	0.08

Composition of clean dry tropospheric air above oceans at mid-latitudes.



Explain why the % by mass and % by volume figures for the composition of dry air (shown below) differ.

Component	% by mass	% by volume
nitrogen, N ₂	75.5	78.1
oxygen, O ₂	23.1	20.9
argon, Ar	1.3	0.9

Check your answer.



- 1 The total mass of the atmosphere is estimated to be 5.1×10^{21} grams. Use this information and the information in the table below to calculate the mass and moles of oxygen and ozone in the atmosphere.

Gas	Formula	Molar mass (g/mol)	Mass in atmosphere (g)	Moles in atmosphere
nitrogen	N ₂	28	$(755000/1\ 000\ 000) \times 5.1 \times 10^{21}$ $= 3.9 \times 10^{21}$	$3.9 \times 10^{21}/28$ $= 1.4 \times 10^{20}$
oxygen	O ₂			
ozone	O ₃			

- 2 Explain why your calculation of the amount of ozone in the atmosphere is not as valid as your calculation of the amount of oxygen

- 3 Compare the amount of oxygen in the atmosphere with the estimated amount of oxygen bound in the Earth's crust – 1.3×10^{24} g.

- 4 Compare the bonding of oxygen in the atmosphere with that of oxygen in the Earth's crust.

Check your answers.

Main air pollutants in the troposphere

Most air pollutants are produced by combustion of fossil fuels in internal combustion engines and electric power stations, burning of plant matter (crop residues, forest fires) and volcanic eruptions. Only major volcanic eruptions are likely to disturb the stratosphere.

Pollutant	Sources	Unhealthy level
carbon monoxide	incomplete combustion, cigarette smoke	> 9 ppm for 8 hours
NO_x	high temperature combustion	> 0.03 ppm for one year
particulate matter (< 10 μm diameter)	incomplete combustion, earthmoving, some mining and industry, some agricultural practices	>50 $\mu\text{g}/\text{m}^3$ for one day
volatile organic compounds (VOC)	solvents, unburnt fuel	varies with compound
sulfur dioxide	burning fossil fuels, metal extraction	>0.02 ppm for one year
lead	leaded petrol, housepaint more than 50 years old	>0.5 $\mu\text{g}/\text{m}^3$ for one year

Volatile organic compounds (VOC) are mostly non-methane hydrocarbons (NMHC). They can vary greatly in their effects – some are carcinogenic (cancer initiating substances).

Methane (CH_4) is present in air in much higher concentrations than non-methane hydrocarbons but is less harmful to human health. Methane has no carbon to carbon bonds and is less reactive than NMHCs.

Gases of concern for their contribution to the enhanced greenhouse effect producing global warming are CO_2 , CH_4 , CFCs (freons) and nitrous oxide N_2O (produced by bacteria particularly in chemically fertilised soils).

Ozone formation in the stratosphere

The strong double bond in a diatomic oxygen molecule O=O can be broken by high energy UV radiation. This produces two oxygen atoms.



The oxygen atoms formed are energetic and collide with diatomic oxygen to form triatomic oxygen, O₃.



The ozone formed in the stratosphere absorbs the medium energy UV that causes skin cancer at ground level. (The medium energy UV carries sufficient energy to break covalent bonds in biological molecules, interrupt normal biological processes and produce chemicals not normally found in organisms. These changes can initiate cancer.)



The oxygen atom produced often has unpaired electrons and is very reactive. The energetic O will react quickly with another O₂ to form more O₃.



Adding the last two equations together the net result is absorption of UV energy and its conversion to heat energy. This explains why the stratosphere temperature increases with altitude. For every ozone molecule that absorbs UV, an energetic O is produced that forms another O₃ molecule. UV energy is converted to heat energy mostly in the upper parts of the stratosphere where the UV enters. The stratosphere is a global inversion layer with warmer air above cooler air. This impedes vertical movement of gases from the troposphere into the stratosphere and within the stratosphere.

Ozone is mostly destroyed when an oxygen atom and ozone molecule react.



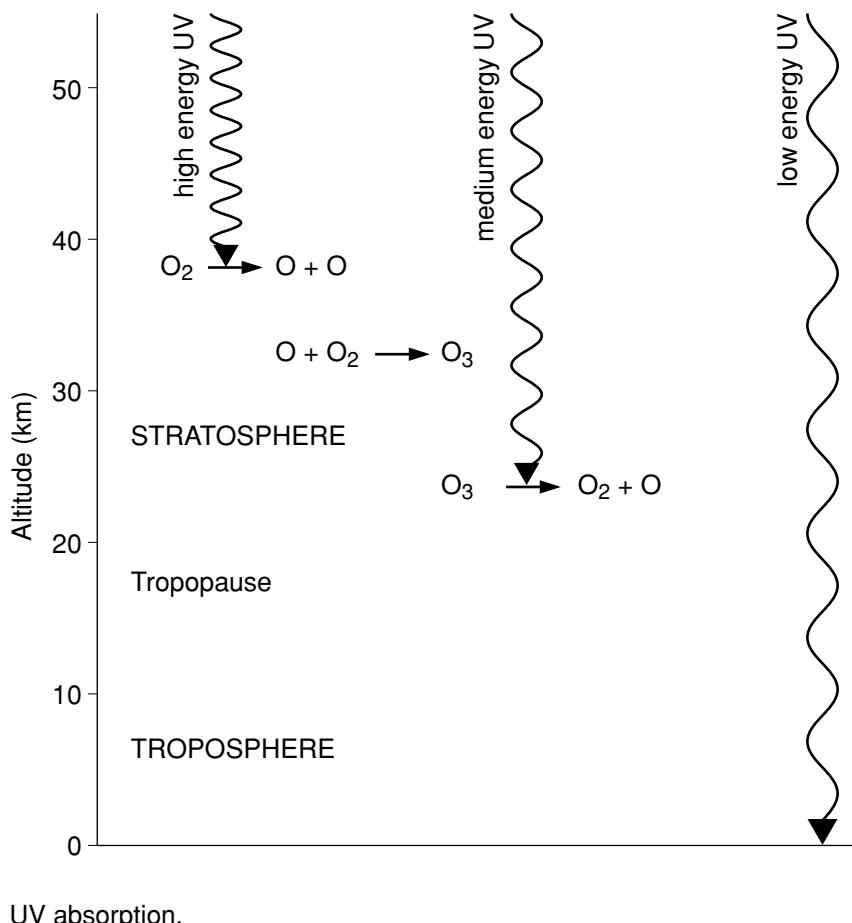
Certain trace species in the stratosphere such as NO, NO₂, Cl and ClO₂ catalyse the formation of O₂ from O₃. In the last 30 years the levels of these trace species have risen and this can be related to decreases in stratospheric ozone – the Earth's UV radiation shield.

On average an ozone molecule has a lifetime of less than a minute before it reacts or is broken down by UV. Fortunately this rapidly destroyed ozone is replaced by newly created ozone and a balance is set up.

The average maximum concentration of ozone in the stratosphere is 10 ppm. The concentration can double or halve according to reactions that depend on the season. Currently there is concern about additional reactions that destroy ozone over Antarctica at the beginning of the southern spring. These additional seasonal reactions lead to what is called the 'ozone hole', a region in the stratosphere of very low ozone concentrations. An ozone hole allows medium energy UV, capable of causing skin cancer, eye damage and plant damage, to reach the Earth's surface.

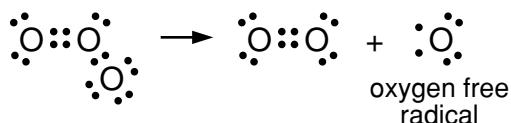
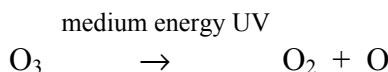
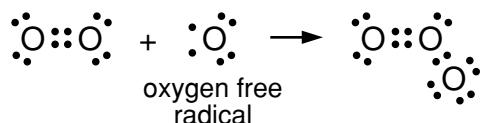
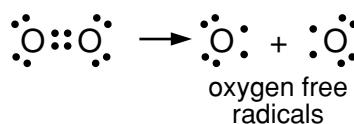
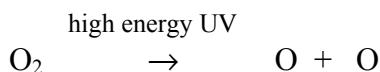


You can see quicktime movies showing the creation and destruction of ozone by referring to the www.lmpc.edu.au/science web site. Go to Chemistry, then module 9.4 for the links.



UV absorption.

Lewis electron dot representations

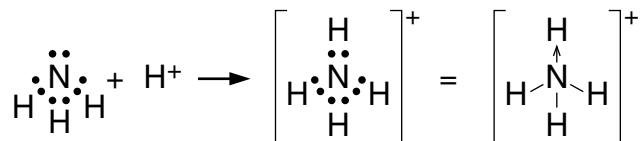


Energy from UV stored in oxygen free radicals is changed to heat energy when they react. Thus, UV energy absorbed in the stratosphere raises the temperature of the stratosphere.

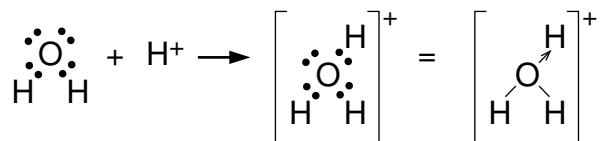
Coordinate covalent bonds

A coordinate covalent bond is a covalent bond in which the shared pair of electrons came from only one of the two atoms joined. An arrow pointing from the atom that provided the shared pair of electrons is used in some diagrams to show a coordinate covalent bond.

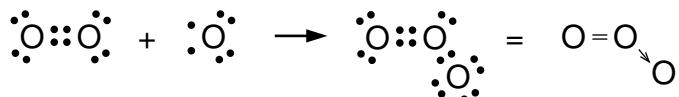
When an ammonia molecule reacts with a hydrogen ion to form an ammonium ion, a coordinate covalent bond forms between the hydrogen nucleus and the nitrogen of the ammonia.



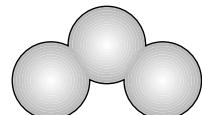
Similarly, when a hydrogen ion attaches to a water molecule to form a hydrated hydrogen ion or hydronium ion, a coordinate covalent bond forms.



In the formation of ozone a coordinate covalent bond forms between the attaching O and the O₂.



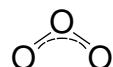
The O₃ molecule has this shape.



Measurements of bond distances indicate no difference in length between the two bonds. The electrons joining the outer atoms to the central atom are delocalised, that is spread evenly, so that the two bonds are the same. Chemists can visualise the ozone molecule as an intermediate form between these two structures.



The delocalised electrons can be represented by dashes.



This diagram shows that the two bonds between oxygens are the same.

Comparing the oxygen allotropes O₂ and O₃

Property	Oxygen	Ozone
molecular formula	O ₂	O ₃
molecular shape	linear	bent
structural formula	O = O	
Lewis dot formula		
MP(°C)	-219	-193
BP(°C)	-183	-111
liquid density (g cm ⁻³)	1.15	1.61
gas colour	colourless	bluish
odour	odourless	pungent
stability to heat	stable	unstable
stability to UV	high - requires high energy UV to decompose	moderate - requires medium energy UV to decompose
chemical reactivity	moderate	high



- 1 Which property indicates that intermolecular forces are greater between ozone than oxygen? Explain your choice.

- 2 Which property suggests that the bond strength between oxygen atoms is greater in oxygen than ozone? Explain your choice.

- 3 Explain why the density of liquid ozone is so much greater than the density of liquid oxygen.

Check your answers.

Comparing O₂ and the oxygen free radical

An oxygen atom can be represented by a Lewis diagram showing all outer electrons paired. The atom is in its lowest energy level or what is called the **ground state**.



When an oxygen molecule is split into two oxygen atoms by high energy UV the oxygen atoms produced are often best represented by

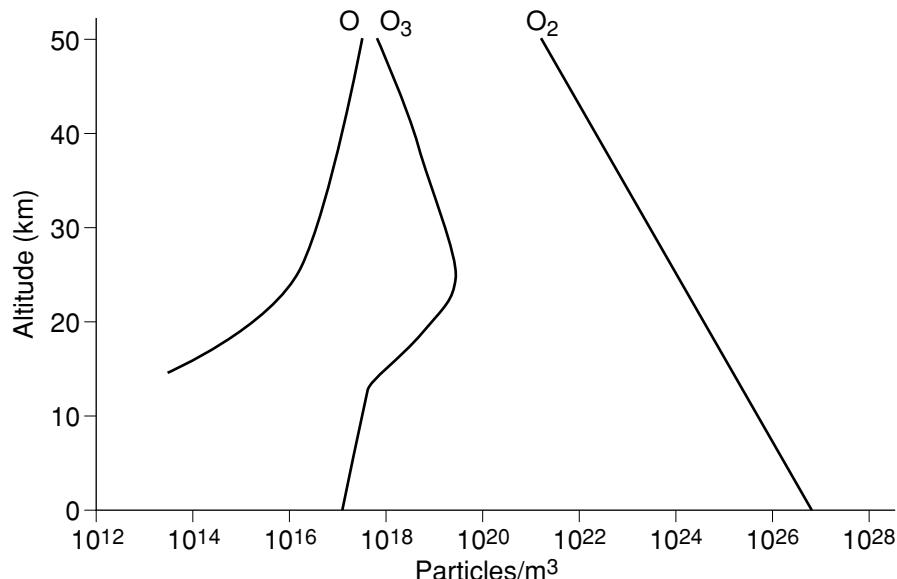


These energetic oxygen atoms have unpaired electrons and are called **free radicals**. They have more than the ground state energy level. This additional energy, as well as the unpaired electrons make these oxygen atoms very reactive.

Diatomic oxygen (O₂) is moderately reactive but the oxygen free radical, like ozone, is highly reactive.



Compare the concentrations of O₂, O₃ and O at different altitudes in the diagram below. Answer the questions based on this diagram.



Concentrations of O, O₃ and O₂.

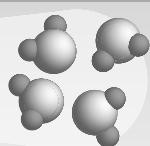
- 1 Explain why the concentration of O is negligible below 15 km altitude.



- 2 a) What altitude has the highest concentration of O₃? _____
 b) What chemical reactions produce this high concentration of O₃? _____

- 3 The percentages of air that is N₂, O₂ and Ar is constant from 0 to 50 km altitude. Add two lines to the graph above showing N₂ and Ar levels.

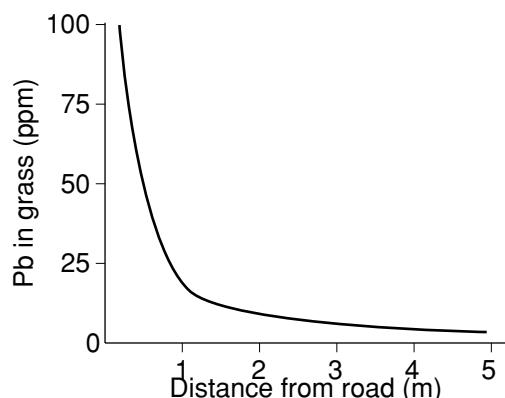
Check your answers.

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Notable scientists

Thomas Midgley Jr. was an American chemist born in 1889. He developed two chemicals of great environmental significance – tetraethyl lead (TEL) and chlorofluorocarbon (CFC). It's worth studying how these chemicals changed from being regarded as environmentally good to environmentally bad.

TEL improved the efficiency of combustion of petrol in internal combustion engines. Less fuel was used, this was an environmental positive. However measurements of lead concentrations near roads revealed data like that shown in the graph below.



Lead concentrations in grass and distance from the road.

Lead and lead compounds accumulate in the human body, particularly in nervous tissue such as the brain. This is an environmental negative.

In the early 1900s liquid ammonia and sulfur dioxide were used as **refrigerants** (liquids which absorb heat from a refrigerator and release the heat through coils to outside air). Accidental escape of these toxic liquids caused many deaths. Midgley developed CFCs to replace these toxic liquids. To demonstrate how harmless CFC was to humans Midgley filled his lungs with CFC then breathed it out to extinguish a candle flame.

CFCs are stable chemicals harmless to humans. Another environmental positive.

What no-one realised was that these inert compounds would be so stable they would not react in the troposphere. Nor could CFCs be washed out of the troposphere by rain because they are water insoluble. Decades after their release these stable chemicals diffuse into the stratosphere. In the stratosphere UV had sufficient energy to break the C–Cl bonds releasing Cl free radicals. It was not until the 1970s that some scientists realised that the CFCs (good in the troposphere) were reducing the ozone UV radiation shield (bad in the stratosphere).

	Troposphere	Stratosphere
Ozone	bad	good
Chlorofluorocarbons	good	bad

Midgely was paralysed by polio in 1940 and died a few years later tangled in the system of ropes and pulleys he had rigged up between his bed and wheelchair.

As a chemist Midgley developed TEL to overcome problems with inefficient petrol combustion and CFCs to replace hazardous refrigerants. Unfortunately TEL produced a lead toxicity problem localised close to traffic while CFCs produced a potentially global problem.

Chemical problems require chemical solutions. Chemists help by:

- alerting society through professional association meetings and publications
- developing alternative chemicals
- monitoring the environment and providing situation management advice.

In the early 1970s the Dutch scientist Paul Crutzen investigated the effect of nitrous oxide N₂O on ozone in the stratosphere. Nitrous oxide is emitted by soil bacteria, particularly when artificial nitrogen fertilisers are used, and from the exhausts of supersonic aircraft such as the Concorde which fly in the lower stratosphere. What Crutzen discovered led to concern about the future of the stratospheric ozone layer.

In the mid 1970s investigations by the Mexican Mario Molina and the American Sherwood Rowland showed that chlorofluorocarbons were even more important than N₂O in stratospheric ozone depletion.

Measurements by British scientists in Antarctica, confirmed by data from American satellite measurements, alerted the world to the dramatic change in the structure of the atmosphere known as the ozone hole.

International conferences involving scientists and politicians lead to the 1987 *Montreal Protocol on Substances That Deplete the Ozone Layer*.

In 1995 Crutzen, Molina and Rowland shared the Nobel Prize for Chemistry.

You will now learn about the mechanism by which good tropospheric CFCs become bad stratospheric CFCs and what has been achieved to date in overcoming the problem.

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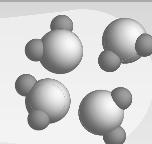
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Haloalkanes

A **haloalkane** is an alkane in which one or more H atoms has been replaced by a halogen (fluoro/chloro/bromo/iodo) atom. About 80% of the Cl in the stratosphere comes from the haloalkanes CFCs.

Chlorofluorocarbons

CFCs were invented in 1928 but large-scale production and use occurred only after 1950. The main uses for CFCs were for refrigerants in refrigerators and air conditioners and as a propellant for aerosol cans.

Examples of CFCs are:

CFC-11 CCl_3F trichlorofluoromethane

CFC-12 CCl_2F_2 dichlorodifluoromethane

CFC-113 $CFCl_2CF_2Cl$ 1,1,2-trichloro-1,2,2-trifluoroethane.

To work out the formula of a CFC add 90 to the code:

eg. for CFC-11: $90 + 11 = 101$

The three digits correspond to the number of C, H and F in that order with the rest of the atoms Cl.

Thus, CFC-11 has one C, no H, one F and the rest Cl.
Hence, $CFCl_3$ (which can also be written as CCl_3F).

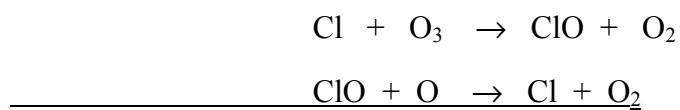
CFCs do not destroy ozone. Products of the UV decay of CFCs in the upper atmosphere such as chlorine atoms and chlorine monoxide, catalyse destruction of ozone. Both the Cl atom and the ClO molecule have an unpaired electron and so are free radicals and very reactive.



Draw Lewis electron dot representations for Cl and ClO. Make sure you have an unpaired electron in each diagram.

Check your answers.

The very reactive Cl and ClO free radicals act as catalysts. They speed up reactions that remove ozone and oxygen free radicals that could form ozone.

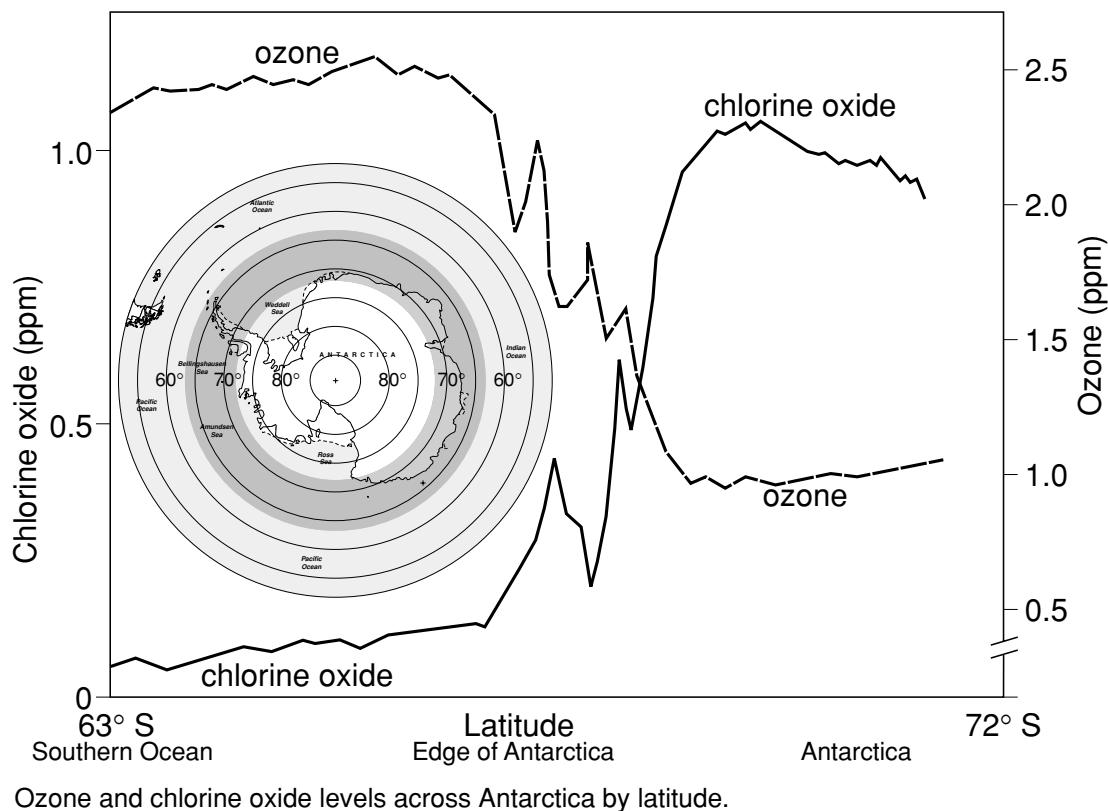


The overall result is: $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$

Each Cl catalyses the destruction of thousands of O_3 molecules!



Explain why this graph is evidence for the involvement of ClO in the destruction of ozone.



Haloalkane replacements for CFCs



R12 (Refrigerant CFC-12) is used in the air conditioner of a 1983 BMW car

CFCs have been temporarily replaced with other haloalkanes called hydrochlorofluorocarbons, HCFCs. The hydrogen enables HCFCs to react with OH free radicals in the troposphere. Reaction is slow and a substantial proportion of HCFCs will still reach the stratosphere.

An example is HCFC-22 (CHClF₂) used as a refrigerant and in home air conditioners. A typical HCFC will destroy 1–10% as much ozone as the same amount of CFC.



Check that the formula for HCFC-22 can also be worked out using the method given for CFCs. (See the box on a previous page).

Check your answers.

Another group of haloalkanes, the hydrofluorocarbons HFCs, are starting to replace some HCFCs. The hydrogen in HFCs encourages their destruction in the troposphere by OH free radicals. Because HFCs contain no chlorine at all they have zero ozone depletion potential if they reach the stratosphere. HFC-134a, CF₃CH₂F, is used in some auto air conditioners and refrigerators.



Refrigerant 134a (HFC-134a) is used in this 1999 car air conditioner.

Use of HFCs still needs to be monitored and managed as they are enhanced greenhouse effect gases and could contribute significantly to global warming.

Halons

Halons are bromofluorocarbons used to extinguish fires in electrical and computer systems. Examples include, bromochlorodifluoromethane, CBrClF_2 and bromotrifluoromethane, CBrF_3 . All yellow fire extinguishers containing halons in Australia should have been withdrawn from use by now.

Halons were produced in much smaller amounts than CFCs but the C–Br bond is weaker than the C–Cl and therefore more easily broken. More importantly on a per atom basis, Br is 10–100 times as destructive of ozone as Cl.

The 1987 Montreal Protocol applies to halons as well as CFCs. The protocol was amended in Copenhagen in 1992 to state that production of CFCs, halons and the solvent CCl_4 (carbon tetrachloride/tetrachloromethane) was to cease entirely by 1996.

Naming straight chain haloalkanes

- 1 Use the prefixes bromo-, chloro-, fluoro-, iodo- in that alphabetic order
- 2 The position of each halogen atom is indicated by a number; number the longest carbon chain from the end that gives the lowest numbers.
- 3 Use the prefixes di-, tri-, tetra- if there is more than one of a type of halogen atom; ignore these prefixes when arranging the halogen atoms in alphabetic order.
- 1 Match the formulas in the first column with the names in the other column by drawing a connecting line between each appropriate formula and name.



CHFClCH ₂ Cl	1,2-dichloro-1-fluoroethane
CHCl ₂ CH ₂ F	1,1-dichloro-1-fluoroethane
CFCl ₂ CH ₃	1,1-dichloro-2-fluoroethane
CHF ₂ CHF ₂	1,1,1,2-tetrafluoroethane
CF ₃ CH ₂ F	1,1,2,2-tetrafluorethane
Cl ₂ FCCClF ₂	1,1,2-trichloro-1,2,2-trifluoroethane
CF ₃ CFCl ₂	2,2-dichloro-1,1,1,2-tetrafluoroethane

- 2 Are the formulas given above structural or molecular? Put the appropriate heading *Structural formula* or *Molecular formula* above the given formulas.
- 3 Isomers have the same molecular formula but different structural formulas. Add another column in front of the first column and complete it so that you can compare molecular formulas and structural formulas.
- 4 Add the codes CFC, HCFC and HFC to the right of the column of names to distinguish chlorofluorocarbons, hydrochlorofluorocarbons and hydrofluorocarbons.

Check your answers.

Isomers

Isomers have the same molecular formula but different structural formulas.

The molecular formula shows how many of each type of atom are in the molecule. The structural formula shows which atoms are joined to which other atoms, that is, the structure of the molecule.

If you are trying to decide if two structural formulas represent different views (eg. front and back) of the same molecule name the structures systematically. If you end up with different systematic names they are isomers. The same systematic name for both structures indicates they are different views of the same molecule.



1 Systematically name each of the following structural formulas.

Structural formula	Systematic name
$\begin{array}{c} \text{F} \\ \\ \text{Cl}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array}$	
$\begin{array}{cc} \text{F} & \text{Cl} \\ & \\ \text{F}-\text{C} & -\text{C}-\text{Cl} \\ & \\ \text{F} & \text{F} \end{array}$	
$\begin{array}{cc} \text{Cl} & \text{Cl} \\ & \\ \text{F}-\text{C} & -\text{C}-\text{F} \\ & \\ \text{F} & \text{F} \end{array}$	
$\begin{array}{c} \text{H} \\ \\ \text{F}-\text{C}-\text{Cl} \\ \\ \text{F} \end{array}$	
$\begin{array}{cc} \text{H} & \text{F} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{F} \\ & \\ \text{F} & \text{F} \end{array}$	

2 Which two names represent isomers?

Check your answers.

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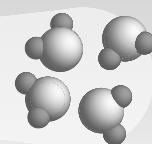
SYMBOLIC

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equations
calculations



MICRO

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interactions



Measuring atmospheric ozone

Ozone concentrations are measured using UV spectrometers on the ground, in balloons, in aircraft or in satellites. The Total Ozone Monitoring Spectrometer, TOMS, in the Nimbus 7 satellite, provided global ozone data almost every day from 1978 to 1993.

Accuracy of TOMS is believed to be within 3 – 4% of actual ozone levels. Extensive checks are made of the equipment and abnormal readings. Adjustments have to be made due to interference by SO_2 ejected from volcanoes. The checking of data outside normal ranges were instrumental in discovering the ozone hole over Antarctica.

The amount of ozone in a column of air above the Earth's surface is measured in Dobson units, DU. One DU is about equal to a 0.01mm thick layer of ozone at sea level or 2.7×10^{16} molecules/cm³. Whole atmosphere ozone measurements are in the range 100 to 500 DU. There are about 3×10^{15} g of ozone in the Earth's atmosphere. About 90% is in the stratosphere.



Considerable information including contour maps showing development of the Antarctic ozone hole can be seen at various websites. Go to www.lmpc.edu.au/science for relevant web sites.

UV radiation, life and polymers

Low energy UV absorbed by molecules can unpair electrons making the molecule more reactive. Low energy UV promotes electrons (especially delocalised electrons) to higher energy levels.

If the promoted electrons fall back to lower energy levels, visible light is emitted. Substances in which this emission occurs almost immediately after absorption of the UV are called **fluorescent**. Fluorescent chemicals line the inside of fluorescent light tubes, are found in laundry powders to brighten the appearance of washed clothes and are in the fabric of white clothing that looks blue under disco lighting.

Low energy UV is used by human skin to make vitamin D. Vitamin D deficiency is virtually unknown in Australia – about five minutes exposure to sunlight is sufficient to make the daily requirement of vitamin D.

Low energy UV changes pale unoxidised granules of skin melanin to dark brown oxidised melanin. If the granules are evenly spread you get a uniform tan. If not, you end up with lots of freckles! If your skin is exposed to more low energy UV the amino acid tyrosine is changed to make more melanin and a longer lasting tan.

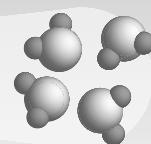
As the energy of the UV is increased (shorter wavelengths) bonds can be broken. Double covalent bonds in particular are likely to change to a single bond and form extra single bonds.

UV can kill cells by damaging the DNA in hereditary material. The UV causes two of the thymine bases in DNA to link. This link makes it difficult for the DNA to replicate and form new cells. There is an enzyme system that removes the linked thymine bases and closes the gap produced. However, with too much damage of this type, the cell cannot carry out its normal functions. The cell may become precancerous or cancerous. Skin cell damage may be apparent within a year or could take 20 to 30 years before it is detected.

High energy UV can damage the surface of polymer materials. The polymer surface becomes brittle, develops cracks and breaks away. Plastic materials such as PVC guttering and water acrylic plastic paint exposed to sunlight often have a lot of inorganic filler such as titanium dioxide added. The filler absorbs the UV energy and minimises polymer damage. The product is often said to be UV stabilised, UV protected or guaranteed for so many years of sunlight exposure.



Complete Exercise 5.1 and 5.2.

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Suggested answers

Composition of the atmosphere

The % by volume figures indicate the proportion of the different molecules in a sample of air. (This follows from Avogadro's Law – equal volumes of gases contain the same number of molecules; if the air is 78.1% nitrogen by volume then nitrogen molecules are 78.1% of the gaseous molecules present).

N_2 molecules of molecular mass 28 are lighter than O_2 of molecular mass 32 and Ar of molecular mass 40. The average molecular mass in air is close to 29 so the mass figure for N_2 is below its volume figure while the gases with molecular masses above 29 have higher % by mass.

1

Gas	Formula	Molar mass (g/mol)	Mass in atmosphere (g)	Moles in atmosphere
nitrogen	N_2	28	$(755\ 000 / 1\ 000\ 000) \times 5.1 \times 10^{21} = 3.9 \times 10^{21}$	$3.9 \times 10^{21} / 28 = 1.4 \times 10^{20}$
oxygen	O_2	32	$(231\ 000 / 1\ 000\ 000) \times 5.1 \times 10^{21} = 1.2 \times 10^{21}$	$1.2 \times 10^{21} / 32 = 0.4 \times 10^{20}$
ozone	O_3	48	$(0.02 / 1\ 000\ 000) \times 5.1 \times 10^{21} = 1.0 \times 10^{14}$	$1.0 \times 10^{14} / 48 = 2.1 \times 10^{12}$

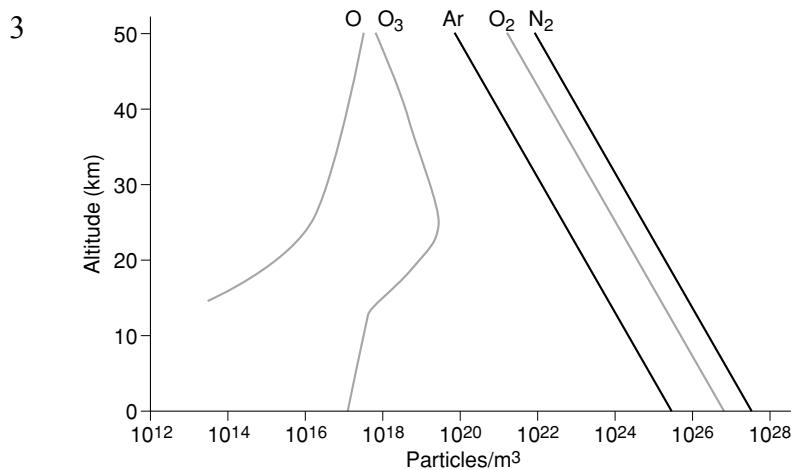
- 2 The figures used for the calculation of ozone assumed the proportion of ozone in the troposphere was the same as in the rest of the atmosphere. The stratosphere is thicker than the troposphere and contains much more ozone.
- 3 Amount of oxygen in the atmosphere is about one thousandth of the amount of oxygen bound in the Earth's crust
- 4 Oxygen in the atmosphere is covalently bonded to other oxygen atoms or other non-metal atoms. In the Earth's crust oxygen is bonded covalently to silicon or ionically to metals.

Comparing the oxygen allotropes O₂ and O₃

- 1 The higher BP for ozone indicates greater intermolecular forces. BP is a better measure than MP because BP is for molecules close together moving over one another. In MP the closeness of packing of molecules is an additional important factor.
- 2 Moderate reactivity of oxygen compared to high reactivity of ozone suggests oxygen has greater bond strength and therefore less reactivity.
- 3 Ozone molecules are not much larger than oxygen molecules and therefore occupy a similar volume. However ozone has $48/32 = 1.5$ times the mass of oxygen and therefore has a density nearly 1.5 times as great.

Comparing O₂ and the oxygen free radical

- 1 O is formed by the action of high energy UV on O₂ but below 15 km there is hardly any of this high energy UV. Gases in the stratosphere are warmer than and therefore less dense than tropopause gases. The stable tropopause also discourages mixing.
- 2 a) 25 km
b) O₂ + high energy UV → 2 O O₂ + O → O₃



Chlorofluorocarbons



As the concentration of ClO increases, the concentration of ozone decreases and vice versa.

Haloalkane replacements for CFCs

$$90 + 22 = 112$$

1 C 1 H 2 F and the rest of the atoms Cl = CHF₂Cl which is the same molecule as CHClF₂.

The method works for HCFCs as well as CFCs.

Naming straight chain haloalkanes

Structural
formulas

C ₂ H ₃ Cl ₂ F	CHFClCH ₂ Cl	_____	1,2-dichloro-1-fluoroethane	HCFC
C ₂ H ₃ Cl ₂ F	CHCl ₂ CH ₂ F	_____	1,1-dichloro-1-fluoroethane	HCFC
C ₂ H ₃ Cl ₂ F	CFCl ₂ CH ₃	_____	1,1-dichloro-2-fluoroethane	HCFC
C ₂ H ₂ F ₄	CHF ₂ CHF ₂	_____	1,1,1,2-tetrafluoroethane	HFC
C ₂ H ₂ F ₄	CF ₃ CH ₂ F	_____	1,1,2,2-tetrafluoroethane	HFC
C ₂ Cl ₃ F ₃	Cl ₂ FC ₂ ClF ₂	_____	1,1,2-trichloro-1,2,2-trifluoroethane	CFC
C ₂ Cl ₂ F ₄	CF ₃ CFCl ₂	_____	2,2-dichloro-1,1,1,2-tetrafluoroethane	CFC

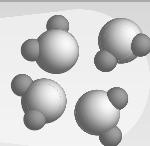
Isomers

1

Structural formula	Systematic name
$\begin{array}{c} \text{F} \\ \\ \text{Cl}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array}$	trichlorofluoromethane
$\begin{array}{ccccc} \text{F} & & \text{Cl} & & \\ & & & & \\ \text{F}-\text{C} & -\text{C}- & \text{Cl} & & \\ & & & & \\ \text{F} & & \text{F} & & \end{array}$	1,1-dichloro-1,2,2,2-tetrafluoroethane
$\begin{array}{ccccc} \text{Cl} & \text{Cl} & & & \\ & & & & \\ \text{F}-\text{C} & -\text{C}- & \text{F} & & \\ & & & & \\ \text{F} & & \text{F} & & \end{array}$	1,2-dichloro-1,1,2,2-tetrafluoroethane

$\begin{array}{c} \text{H} \\ \\ \text{F}-\text{C}-\text{Cl} \\ \\ \text{F} \end{array}$	chlorodifluoromethane
$\begin{array}{cc} \text{H} & \text{F} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{F} \\ & \\ \text{F} & \text{F} \end{array}$	1,1,1,2-tetrafluoroethane

- 2 1,1-dichloro-1,2,2,2-tetrafluoroethane and 1,2-dichloro-1,1,2,2-tetrafluoroethane are both isomers of $\text{C}_2\text{F}_4\text{Cl}_2$.

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Exercises – Part 5

Exercises 5.1 to 5.2

Name: _____

Exercise 5.1: Alternative chemicals to replace CFCs

- 1 Identify two types of alternative chemicals used to replace CFCs.

- 2 Evaluate (make a judgement based on criteria) the effectiveness of their use as a replacement for CFCs.

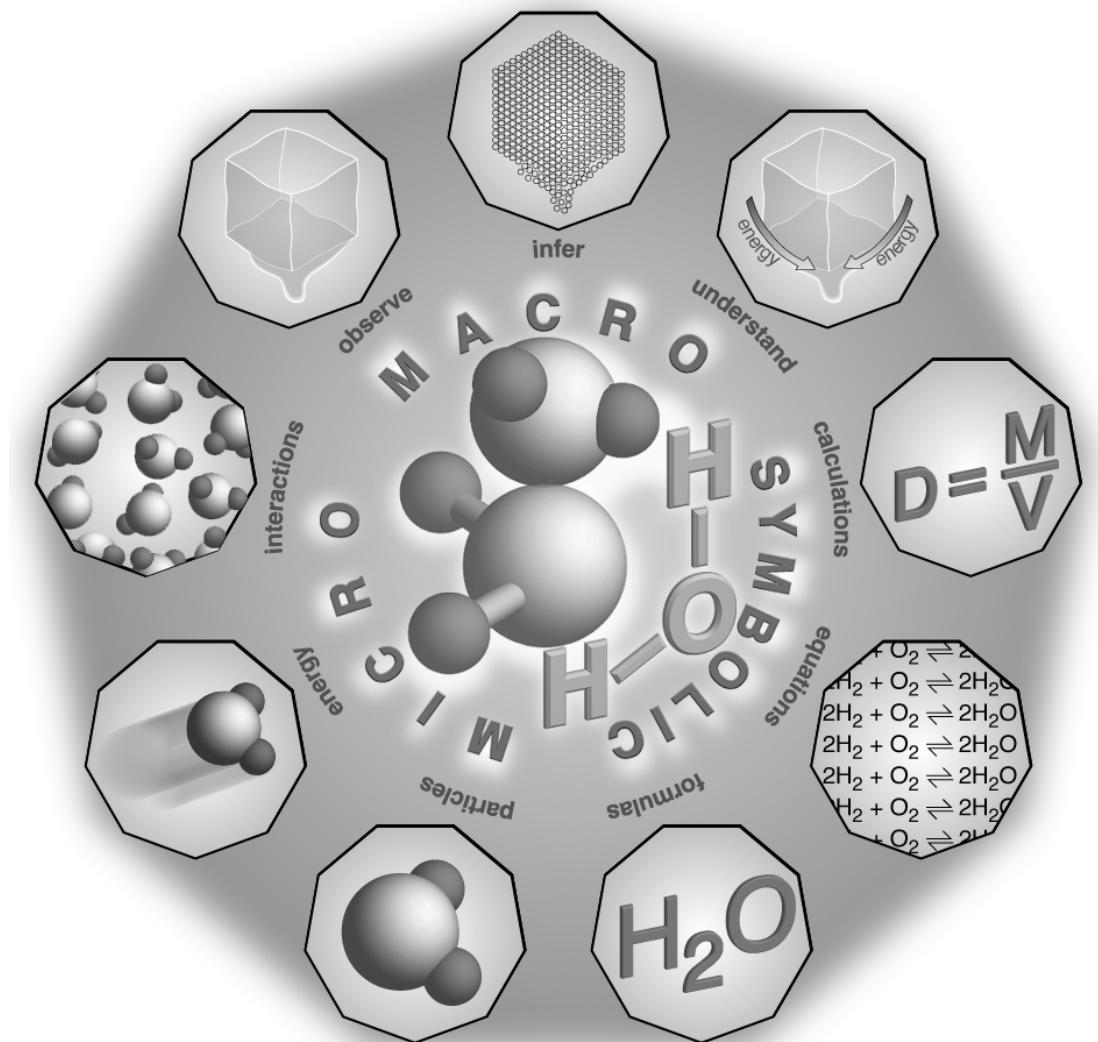
Exercise 5.2: An Australian scientist's contribution

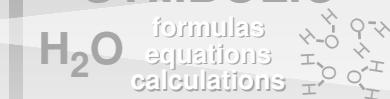
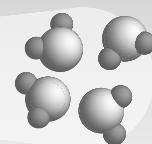
Jonathan Banks is an Australian scientist who has received international awards for his contributions towards the problem of stratospheric ozone depletion. Find out what you can about his contribution and list the sources of your information.



Chemical monitoring and management

Part 6: Key ideas, key words and outcomes



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Contents

Introduction	2
Key ideas	3
Monitoring and managing water quality	3
Chemists at work.....	4
Haber-Bosch process.....	4
Chemical analysis	5
CFCs and ozone	5
Key words	6
Aspirin, Aspro and Disprin	7
Nobel prize winners in chemistry.....	10
Suggested answers.....	13
Exercises – Part 6	19

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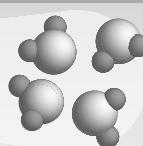
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Introduction

In this part you will:

- review the first five parts of the module by answering true/false statements and explaining why some are false
- revise and apply key words which are important in correctly responding to questions
- revise knowledge and understanding outcomes.

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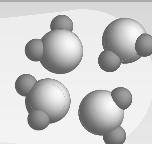
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Key ideas

Assess your understanding of this module by answering these true/false statements one part at a time. Write T or F at the end of each statement. Approximately half the statements are true. If you decide the statement is false, rewrite the statement so that it is true.

Monitoring and managing water quality

- Before total dissolved solids (TDS) of a water sample is measured the sample must be filtered.
- The BOD measured for a water sample can be larger than the DO
- The pH of sea water is normally acidic.
- The pH of rainwater is normally acidic.
- The presence of ions in water reduces the concentration of dissolved oxygen.
- If a 10 cm depth of sample A allows as much light through as a 40 cm depth of sample B then sample A is the least turbid.
- Whether a metal hydroxide precipitates depends on the pH of the solution.
- Screening of drinking water is a physical process.
- Disinfection of drinking water by the addition of chlorine is a physical process.
- Filtration of drinking water by membrane filters is a chemical process.

Chemists at work

- The qualifying body in Australia for professional chemists is the Royal Australian Chemical Institute.
- The major area in which chemists work is analytical chemistry.
- AAS stands for atomic absorption spectroscopy.
- AAS uses a hollow cathode lamp with the cathode made of the metal of interest.
- AAS would be a suitable technique to measure fluoride concentration in drinking water.
- Measuring the oxygen levels in car exhaust gas is an example of management.
- Adjusting the levels of fuel and air using information from an oxygen sensor is an example of monitoring.
- An analytical chemist does not need to know how the samples being analysed were collected.
- An absorption spectrum consists of coloured lines on a dark background.
- AAS for an element measures the amount of absorption of one wavelength of light.

Haber-Bosch process

- The main use of ammonia is as a fertiliser.
- The reaction of nitrogen with hydrogen to form ammonia is an endothermic, reversible reaction.
- Increasing pressure increases the yield of ammonia.
- Increasing temperature increases the yield of ammonia.
- Haber and Bosch shared a Nobel prize for chemistry.
- The main metal used as a catalyst in the Haber process is iron.
- Ammonia is used to make nitric acid which is important in the manufacture of explosives.
- Ammonia is separated from unreacted nitrogen and hydrogen by cooling the mixture.
- CO₂ is absorbed by base solution because it is a basic gas.
- A major advantage of the Haber-Bosch process is that its reactants are obtained from the air at no cost.

Chemical analysis

- The two main methods of classical or 'wet' quantitative analysis are gravimetric and volumetric analysis.
- A flame test is a quantitative test.
- Sulfate ion concentration can be measured by precipitation of BaSO_4 because barium sulfate is very insoluble.
- To measure the nitrogen content of a fertiliser the nitrogen must be separated as nitrogen gas.
- Flame tests can be used to distinguish certain anions.
- Phosphorus content of a detergent requires that the phosphorus is separated as the element.
- Identification of ions in a mixture is mostly based on separation of and colour of precipitates.
- Phosphate, sulfate, carbonate and chloride ions are all colourless.
- Barium, calcium and lead ions are all colourless.
- Colourless ions which combine to form an insoluble salt give a white precipitate.

CFCs and ozone

- Dichlorodifluoromethane is a CFC.
- Dichlorofluoromethane is a HFC.
- Difluoromethane is a HCFC.
- All single oxygen atoms are oxygen free radicals.
- Diatomic oxygen is more reactive than triatomic oxygen.
- Ozone formation in the stratosphere requires UV.
- Ozone formation in the troposphere is beneficial to humans.
- A coordinate covalent bond consists of one electron from each joined atom.
- Isomers have the same molecular formula but different structural formulas.
- Some UV radiation has sufficient energy to break covalent bonds.

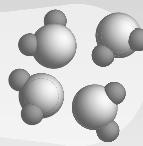
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Key words

Key words indicate how you should answer a question. It is important that you know how to respond to these key words.

You have already seen some key words in the outcome statements:

analyse	identify components and the relationship between them; draw out and relate implications
assess	make a judgement of value, quality, outcomes, results or size
describe	provide characteristics and features
evaluate	make a judgement based on criteria; determine the value of
explain	give cause and effect; make the relationships between things evident; give reasons
identify	recognise and name
justify	support an argument or conclusion with reasons
predict	suggest what might happen

Additional key words you should correctly respond to are:

account for	state the reasons for
compare	show how things are similar or different (by words/labelled diagrams/ table.)
discuss	identify issues and provide points for and/or against
outline	give the main features of

The following activity requires you to:

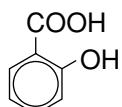


- 1 read about aspirin and other pain relief drugs
- 2 answer questions, about what you have read, that use key words
- 3 read through tables of Nobel prize winners in chemistry
- 4 answer questions, about the table content, that use key words.

Aspirin, Aspro and Disprin

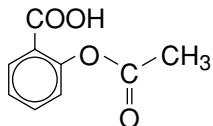
Malaria is normally thought of as a tropical disease but until large scale swamp drainage, malaria was a problem in many parts of the temperate world such as in Europe. In the 1700s it was found that bark of the willow tree could relieve malarial fever.

Extracts of willow bark were first used in the 1800s to relieve rheumatism. By 1870 the active ingredient in willow bark had been identified as salicylic acid.



Salicylic acid relieved fevers and pain but caused irritation of the mouth, oesophagus and stomach. The sodium salt of salicylic acid, sodium salicylate caused less irritation but the taste and the vomiting it caused!

The dominant chemical industry of the late 1800s was in Germany. In the 1890s the Bayer company found that an ester of salicylic acid, acetylsalicylic acid, caused less irritation and tasted a lot better than salicylic acid. Bayer sold the product in 1899 as a patented medicine under the name Aspirin.



In 1914 the British government was unable to obtain supplies of aspirin. A prize was offered throughout the British Empire for any one who could develop a way of making acetylsalicylic acid. George Nicholas, a pharmacist from Melbourne, Australia won the prize. The tablets he made were called Aspro.

The **patents**, exclusive rights to use methods developed to make acetylsalicylic acid, expired long ago for both the Bayer company and the Aspro company. Today over 50 000 tonnes of acetylsalicylic acid is made each year in laboratories throughout the world. It is extensively used for pain relief, reducing fever and reduction of blood clotting. Like all drugs aspirin can be misused and is one of the most frequent causes of accidental poisoning in children.

The World Health Organisation (WHO) defines a drug as a substance which, when taken into the body, alters its function physically or psychologically, excluding food, water and oxygen.

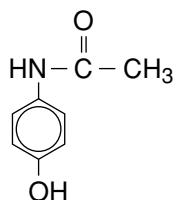
Acetylsalicylic acid is a molecule and has low water solubility. Most aspirin sold in developed countries is sodium acetylsalicylate. This salt form is ionic and more water soluble than molecular acetylsalicylic acid. Disprin™ is a soluble aspirin.

In the acid environment of the stomach the high concentration of hydrogen ions converts the charged acetylsalicylate ion to neutral acetylsalicylic acid molecules. The neutral molecule can pass through the non-polar fat layer that lines the stomach and into the blood.

Aspirin is not recommended for children under six, should be used only under medical supervision with older children and can cause stomach ulcers in susceptible adults. Other drugs have been developed for pain relief.

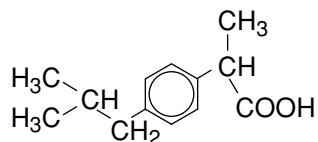
Paracetamol has been available since the 1950s under the established brand name Panadol™.

Because the company Sterling-Winthrop held patents on the manufacture of paracetamol it received payments from other companies using their method of manufacture. A patent expires after a certain length of time (typically 17–20 years for chemical patents). Other companies can then make that chemical without payment to the originator of the method. Like aspirin about 50 000 tonnes of paracetamol is manufactured throughout the world each year.



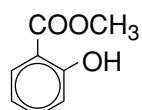
Paracetamol provides safer pain relief than aspirin for children and people with stomach ulcers. However, chronic use can cause liver damage.

In the 1980s ibuprofen became available for pain relief. Ibuprofen causes fewer problems than aspirin and paracetamol.



Aspirin, paracetamol and ibuprofen are swallowed for pain relief.

Methyl salicylate is applied externally to ease the pain of strained muscles and rheumatism. Because this ester is a neutral molecule it can pass through the fat layers of the skin and into muscles and joints.



- 1 Compare the structures of molecules of the pain relievers aspirin, paracetamol and ibuprofen.

- 2 Evaluate the use of drugs in ionic structure rather than molecular structure.

- 3 Justify the restrictions on the sale of drugs through pharmacies only.

- 4 Account for the variation in prices and availability of pain relief drugs.

- 5 Discuss why the British government was unable to obtain aspirin supplies in 1914.

Check your answers.

Nobel prize winners in chemistry

Year	Name	Country of birth	Awarded for
2000	Alan Heeger	US	discovery and development of electrically conductive polymers
	Alan MacDiarmid	New Zealand	
	Hideki Shirakawa	Japan	
1999	Ahmed Zewail	Egypt	studies of the transition states of chemical reactions using femtosecond spectroscopy
1998	Walter Kohn	Austria	developing methods for theoretical study of molecules
	John Pople	UK	
1997	Paul Boyer and John Walker	US	enzyme mechanism for synthesis of ATP
		UK	
	Jens Skou	Denmark	first discovery of an ion-transporting enzyme
1996	Robert Curl	US	discovery of fullerenes
	Harold Kroto	UK	
	Richard Smalley	US	

1995	Paul Crutzen	Holland	work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone
	Mario Molina	Mexico	
	Sherwood Roland	US	
1994	George Olah	Hungary	contribution to carbocation chemistry
1993	Kary Mullis	US	invention of the polymerase chain reaction
	Michael Smith	UK	protein studies
1992	Rudolph Marcus	Canada	theory of electron transfer

Nobel prize winners in chemistry 2000-1992.

Year	Name	Country of birth	Awarded for
1901	Jacobs van't Hoff	Holland	behaviour of moving particles in dilute solutions
1902	Emil Fischer	Germany	sugar and purine synthesis
1903	Svante Arrhenius	Sweden	theory of ionic dissociation in water solutions
1904	William Ramsay	UK	discovery of inert gas elements
1905	Adolf von Baeyer	Germany	work on organic dyes
1906	Henri Moisson	France	isolation of fluorine
1907	Eduard Buchner	Germany	discovery of fermentation outside living cells
1908	Ernest Rutherford	New Zealand	studies of radioactivity, alpha particles and the atom
1909	Wilhelm Ostwald	Germany	work on catalysis

Nobel prize winners in chemistry 1901-1909.



- 1 Assess the importance of country of birth in the awarding of Nobel prizes in chemistry at the beginning and end of the twentieth century.

- 2 Outline the importance of the work that led to the awarding of the 1995 prize.

- 3 Predict the likelihood that the 2001 prize will be awarded for work related to biological chemistry.

- 4 Identify the Nobel prize winning chemist whose work involves measuring very small time intervals.

- 5 Nobel prizes awarded for chemistry at the beginning of the last century were all awarded to one person. With the exception of the New Zealander Ernest Rutherford who worked in England, their work was carried out in their country of birth.

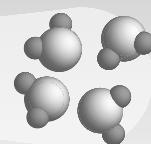
In contrast prizes awarded at the end of the twentieth century were mostly shared and although about one-third of the prize winners were born in the US about two-thirds were living in the US at the time of their award.

Analyse this situation and its implications for young Australian scientists.

Check your answers.



Complete Exercise 6.1 now.

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Suggested answers

Monitoring and managing water quality

- Before total dissolved solids (TDS) of a water sample is measured the sample must be filtered. T
- The BOD measured for a water sample can be larger than the DO. F

BOD is the reduction in DO over a period of time (usually five days) and so is less than or equal to DO.

- The pH of sea water is normally acidic. F
The pH of sea water is slightly alkaline.
- The pH of rain water is normally acidic. T
- The presence of ions in water reduces the concentration of dissolved oxygen. T
- If a 10 cm depth of sample A allows as much light through as a 40 cm depth of sample B then sample A is the least turbid. F

Sample A is 40/10 , that is, four times as turbid as sample B.

- Whether a metal hydroxide precipitates depends on the pH of the solution. T
- Screening of drinking water is a physical process. T
- Disinfection of drinking water by the addition of chlorine is a physical process. F

Chlorine forms chemicals which react with organisms killing them.

- Filtration of drinking water by membrane filters is a chemical process. F

This is a physical process that physically separates particles according to size.

Chemists at work

- The qualifying body in Australia for professional chemists is the Royal Australian Chemical Institute. T
- The major area in which chemists work is analytical chemistry. T
- AAS stands for atomic adsorption spectroscopy. F
AAS stands for atomic absorption spectroscopy.
- AAS uses a hollow cathode lamp with the cathode made of the metal of interest. T
- AAS would be a suitable technique to measure fluoride concentration in drinking water. F
AAS can only be used for solid elements (usually metals) that can be used to make a hollow cathode.
- Measuring the oxygen levels in car exhaust gas is an example of management. F
Measuring is part of monitoring.
- Adjusting the levels of fuel and air using information from an oxygen sensor is an example of monitoring. F
This handling, direction and control of a situation is management.
- An analytical chemist does not need to know how the samples being analysed were collected. F
It is important that the chemist knows the condition under which the samples were collected as this can affect the results.
- An absorption spectrum consists of coloured lines on a dark background. F
Absorption spectrum consists of dark absorption lines on a spectrum background.
- AAS for an element measures the amount of absorption of one wavelength of light. T

Haber-Bosch process

- The main use of ammonia is as a fertiliser. T
- The reaction of nitrogen with hydrogen to form ammonia is an endothermic, reversible reaction. F
The reaction is exothermic.
- Increasing pressure increases the yield of ammonia. T

- Increasing temperature increases the yield of ammonia. F
The reaction is exothermic so increasing the energy available shifts the equilibrium position in the direction of the reactants.
- Haber and Bosch shared a Nobel prize for chemistry. F
Haber and Bosch received their Nobel prizes separately in different years.
- The main metal used as a catalyst in the Haber process is iron. T
- Ammonia is used to make nitric acid which is important in the manufacture of explosives. T
- Ammonia is separated from unreacted nitrogen and hydrogen by cooling the mixture. T
- CO₂ is absorbed by base solution because it is a basic gas. F
CO₂ is an acidic gas and this is why it reacts with base solution.
- A major advantage of the Haber-Bosch process is that its reactants are obtained from the air at no cost. F
Nitrogen is obtained from the air at no cost but the hydrogen comes from fossil fuels such as natural gas or petroleum. The cost of ammonia production is affected by the cost of natural gas/petroleum.

Chemical analysis

- The two main methods of classical or 'wet' quantitative analysis are gravimetric and volumetric analysis. T
- A flame test is a quantitative test. F
A flame test finds out what element is present not how much.
- Sulfate ion concentration can be measured by precipitation of BaSO₄ because barium sulfate is very insoluble. T
- To measure the nitrogen content of a fertiliser the nitrogen must be separated as nitrogen gas. F
The nitrogen can be separated as ammonia and the nitrogen content calculated from the proportion of nitrogen in ammonia.
- Flame tests can be used to distinguish certain anions. F
Flame tests can be used to distinguish certain metal cations.
- Phosphorus content of a detergent requires that the phosphorus is separated as the element. F
The phosphorus can be separated as phosphate and the phosphorus content calculated from the proportion of phosphorus in phosphate.
- Identification of ions in a mixture is mostly based on separation of and colour of precipitates. T

- Phosphate, sulfate, carbonate and chloride ions are all colourless. T
- Barium, calcium and lead ions are all colourless. T
- Colourless ions which combine to form an insoluble salt give a white precipitate. T

CFCs and ozone

- Dichlorodifluoromethane is a CFC. T
- Dichlorofluoromethane is a HFC F
 Cl_2FHC is a hydrochlorofluorocarbon not a hydrofluorocarbon.
- Difluoromethane is a HCFC. F
 F_2H_2C is a hydrofluorocarbon not a hydrochlorofluorocarbon.
- All single oxygen atoms are oxygen free radicals. F
Only energetic oxygen atoms which have enough energy to separate paired electrons are free radicals.
- Diatomic oxygen is more reactive than triatomic oxygen. F
 O_2 is less reactive than O_3 .
- Ozone formation in the stratosphere requires UV. T
- Ozone formation in the troposphere is beneficial to humans. F
Ozone in the troposphere can cause breathing problems, damage materials and affect plant crops.
- A coordinate covalent bond consists of one electron from each joined atom. F
One of the joined atoms contributes both the electrons.
- Isomers have the same molecular formula but different structural formulas. T
- Some UV radiation has sufficient energy to break covalent bonds. T

Aspirin, Aspro and Disprin

- 1 *The structures of all three pain relievers are similar in containing a benzene ring and a methyl group on a side chain near a $C=O$ group. Aspirin and ibuprofen contain an acid $COOH$ group while paracetamol and ibuprofen are similar in having groups attached to the benzene ring at opposite ends of the ring. Differences include the positioning of the two attached groups on adjoining carbon atoms in aspirin, a nitrogen in paracetamol and branched side chains in ibuprofen.*

(In the US paracetamol is called acetaminophen. This name shows that paracetamol contains an acetyl group CH_3CO , an amino group NH and a benzene ring [phen].)

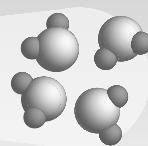
(In paracetamol the para indicates attached groups are on opposite sides of a benzene ring and -ol indicates a OH group.)

- 2 Ionic structure drugs are more soluble in the water of blood and cells because they are polar. Molecular structure drugs are less water soluble but more able to penetrate the fat layers of the skin and protective coating on the inside wall of the stomach. The structure chosen for a drug could depend on its chemical stability and the way in which it is to enter the body.
- 3 Drugs sold through pharmacies must meet quality control standards and have been scientifically tested and observed for side effects and complications. Information on dosage and use is provided with the drug and the pharmacist acts as a resource person for health guidance. This contrasts with the way drugs are sold illegally.
- 4 If a drug is still in patent the company owning the patent has rights to the manufacture and sale of the drug. This enables them to obtain a price to recover research, development and approval costs for the drug. Once the drug is out of patent any manufacturer can make the drug and a more competitive market brings lower costs.
- 5 In 1914 the British government was at war with Germany. Just as the British prevented the movement of nitrogen salts into Germany stimulating development of the Haber process so the Germans did not allow movement of aspirin to Britain.

Nobel prize winners in chemistry

- 1 At the beginning of the twentieth century all prizes were awarded to Europeans and a New Zealander working in Europe.
At the end of the twentieth century prizes were awarded approximately one-third to Europeans, one-third to US and the remainder to a variety of nationalities.
- 2 In the early 1970s Paul Crutzen alerted the scientific community to the destruction of stratospheric ozone by nitrous oxide. In the mid 1970s the work of Mario Molina and Sherwood Roland showed that CFCs were even more important in stratospheric ozone depletion. The work of these Nobel prize winners alerted the world to the damage that was occurring to the UV radiation shield of stratospheric ozone. International conferences and agreements followed to protect the ozone layer.
- 3 The Human Genome Project and biotechnology developments depend on applications of knowledge and understanding of chemistry. Major advances in these areas increase the likelihood that a chemistry Nobel prize will be awarded for supporting work.

- 4 Ahmed Zewail's work using femtosecond spectroscopy enables chemist to see changes that occur 10^{-15} seconds apart as chemicals react.
- 5 The sharing of Nobel prizes for chemistry illustrates increased collaboration and communication between scientists. It could also illustrate increased competition between scientific teams trying to solve the same problems. Scientists today have increased opportunities to carry out research in different countries. They are attracted by financial incentives, laboratory support equipment and opportunities to parts of the world such as the US which invest more in research and development. The international nature of modern science and globalisation make it more likely that young Australian scientists will spend at least part of their working life overseas.

MACROobserve
infer
understand**SYMBOLIC** H_2O formulas
equations
calculations**MICRO**particles
energy
interactions

Exercises – Part 6

Exercise 6.1

Name: _____

Knowledge and understanding outcomes H6 – H10

The questions in this exercise enable you to fulfill the knowledge and understanding outcomes of the HSC chemistry course. All questions are based upon applying the outcomes to work you have done in this module. They require knowledge and understanding of Preliminary work as well as other HSC core modules.

H6 explains reactions between elements and compounds in terms of atomic structures and periodicity

1 Explain why :

- a) high energy oxygen atoms are so reactive using Lewis electron dot diagrams

- b) NO is more reactive than NO_2 using Lewis electron dot diagrams

- c) Ba^{2+} and Ca^{2+} reactions are so similar using periodicity

- d) bond energies are in the order $C-F > C-Cl > C-Br > C-I$ using periodicity.

H7 describes the chemical basis of energy transformations in chemical reactions

- 2 Explain why N₂ and H₂ react more quickly in the presence of iron catalyst.

- 3 Describe why nitrogen-fixing bacteria in certain plant roots can produce NH₃ from N₂ gas at low temperatures and normal atmospheric pressure.

H8 assesses the range of factors which influence the type and rate of chemical reactions

- 4 Assess the range of factors which influence the rate of reaction between gaseous N₂ and gaseous H₂ in the Haber-Bosch process.

- 5 Assess the range of factors which influence whether ions of opposite charge will form a precipitate when their solutions are mixed.

H9 describes and predicts reactions involving carbon compounds

6

Bond type	C–H	C–F	C–Cl	C–Br	C–I
Bond energy (kJ mol ⁻¹)	414	485	327	285	228

A hydrochlorofluorocarbon (HCFC) molecule is exposed to low energy UV radiation. The energy of the UV is slowly increased (that is, the wavelength of emitted UV is slowly decreased).

Predict and describe the order in which atoms will break off the carbon backbone of the HCFC molecules. Explain why you predicted this order.

H 10 analyses stoichiometric relationships

- 7 Addition of varying amounts of 0.200 mol L^{-1} Ba^{2+} to 1.0 L samples of drinking water produced the following amounts of BaSO_4 precipitate.

Volume of 0.200 M Ba^{2+} added (mL)	Mass of BaSO_4 precipitate (g)
1.0	0.047
2.0	0.089
3.0	0.132
4.0	0.178
5.0	0.232
6.0	0.234
7.0	0.231

- a) Predict the mass of precipitate for the addition of 8.0 mL.

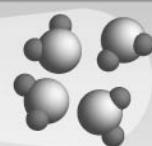
- b) Write a balanced equation for the precipitate formation.

- c) The limiting reactant is the reactant that is used up entirely when a reaction occurs. The limiting reactant limits how much product can be formed. What is the limiting reactant for the formation of precipitate:

- i) when 3.0 mL of 0.200 M Ba^{2+} is added to 1.0 L of drinking water?

- ii) when 6.0 mL of 0.200 M Ba^{2+} is added to 1.0 L of drinking water?

- d) Calculate the concentration of sulfate ions in the drinking water.

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Student evaluation of module

We need your input! Can you please complete this short evaluation to provide us with information about this module. This information will help us to improve the design of these materials for future publications.

1 Name: _____

2 Location: _____

3 Did you find the information in the module easy to understand?

4 Were the instructions clear? _____

5 What did you most like learning about? Why?

6 Which sort of learning activity did you enjoy the most? Why?

7 Did you complete the module within 30 hours? (Please indicate the approximate length of time spent on the module.)

- 8 Do you have access to the appropriate resources? eg a computer, the internet, scientific equipment, chemicals, people that can provide information and help with understanding science

Please return this information to your teacher, who will pass it along to the materials developers at OTEN – DE.

