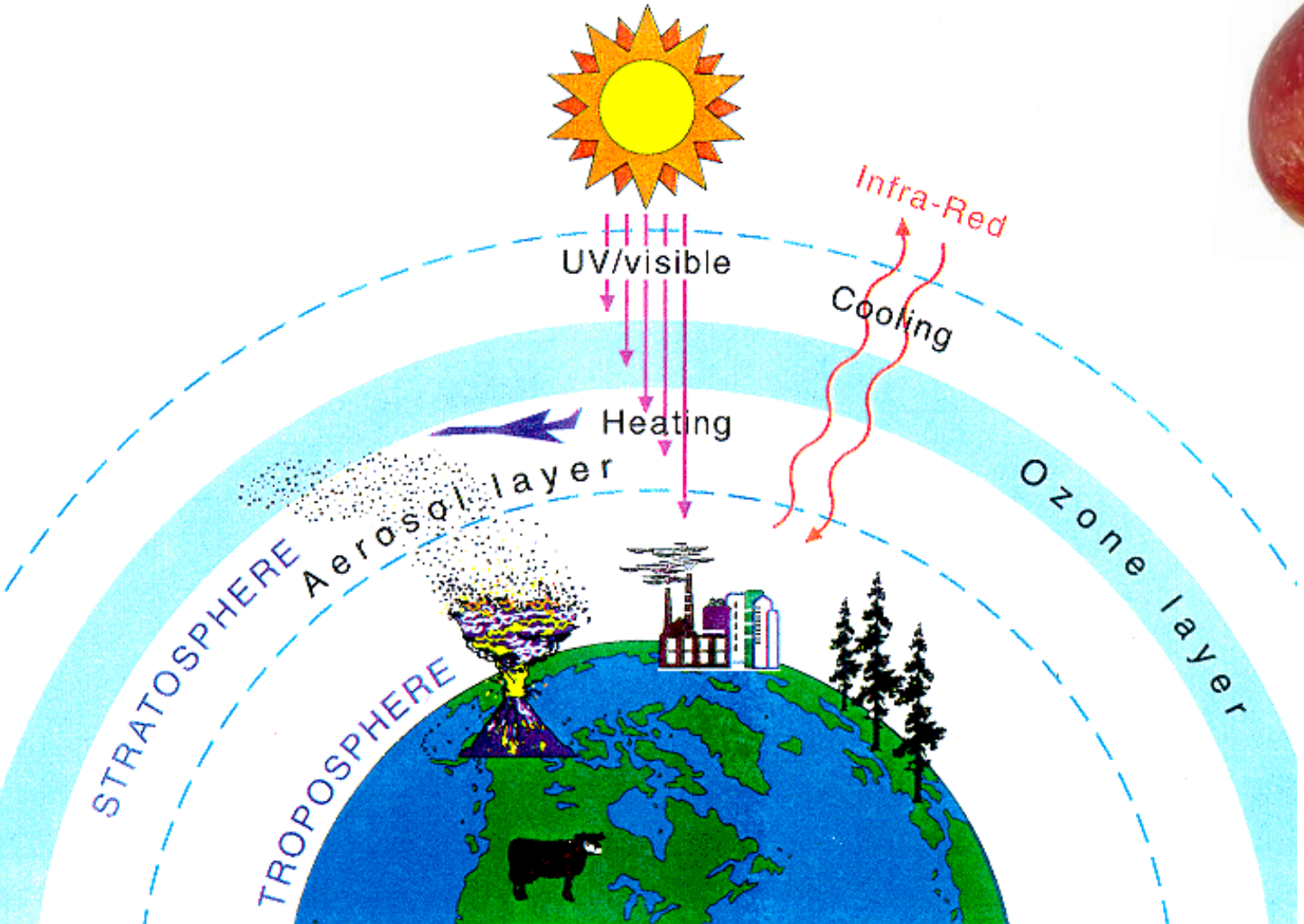
# Chemical Monitoring and Management (Part 2)

***1) Chemistry and the Atmosphere***

***2) Monitoring Water Quality***

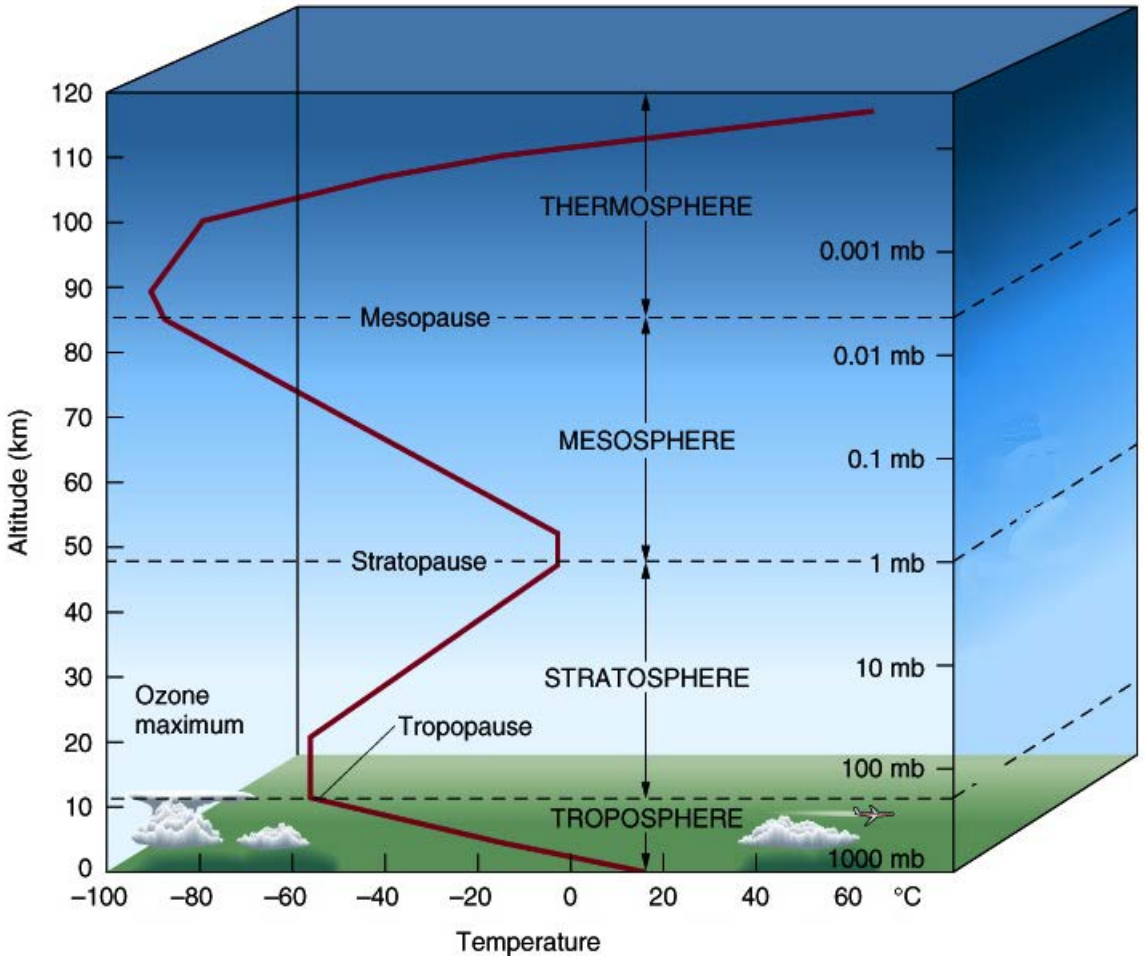
Alexander Comerford
Bachelor of Medical Sciences

# Chemistry and the Atmosphere




If the Earth were the size of an apple, the apple's skin and the atmosphere would be approximately the same thickness.

# Structure of the Atmosphere



# Composition of the Dry* Atmosphere

- Most abundant element in the atmosphere is nitrogen
- Nitrogen, oxygen and argon make up 99.9% of atmosphere
- Most chemistry happens within the other 0.1% ($CO_2$, Ozone etc.)

| Gas | Formula | %Volume |
|---|---|---|
| Constant Gases – Concentrations do not vary significantly | | |
| nitrogen | $N_2$ | 78.1 |
| oxygen | $O_2$ | 20.95 |
| argon | Ar | 0.93 |
| neon | Ne | 0.0018 (18 ppm) |
| helium | He | 0.00052 (5.2 ppm) |
| krypton | Kr | 0.0001 (1 ppm) |
| hydrogen | $H_2$ | 0.00005 (0.5 ppm) |
| xenon | Xe | 0.0000008 (8 ppb) |
| Variable Gases – Concentrations vary | | |
| water | $H_2O$ | 0 - 4 |
| carbon dioxide | $CO_2$ | 0.04 (380 ppm) |
| methane | $CH_4$ | 0.00018 (1.8 ppm) |
| nitrous oxide (laughing gas) | $N_2O$ | 0.0000315 (315 ppb) |

# Atmospheric Pollutants

| POLLUTANT | SOURCE |
|---|---|
| Carbon monoxide (CO) | Energy production |
| Ozone ($O_3$) | Photochemical smog |
| $NO_x$ ($NO$, $NO_2$) | Energy production |
| Hydrocarbons and volatile organic compounds (VOCs) | Manufacturing (glues and solvents), energy production, propellants |
| $SO_x$ ($SO_2$, $SO_3$) | Energy production, ore extraction, volcanoes |
| Chlorofluorocarbons (CFCs) | Before 1996 from fire extinguishers, refrigerants, foam plastics |

# Ozone in The Atmosphere

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- Ozone, $O_3$, is naturally present in the atmosphere
- In the stratosphere, where it can reach up to 12 ppm, it absorbs most of the biologically damaging UV-B radiation from the sun
- It is poisonous to humans and other living organisms and near ground level in clean air it is about 0.02 ppm
- Human activity is producing ozone at ground level where we do not want it and destroying it in the stratosphere where we do want it!

# HSC Multiple Choice (2014)

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***In which layer of the atmosphere is ozone considered a pollutant?***

A. Mesosphere
B. Stratosphere
C. Thermosphere
D. Troposphere

# Ozone Structure and Properties

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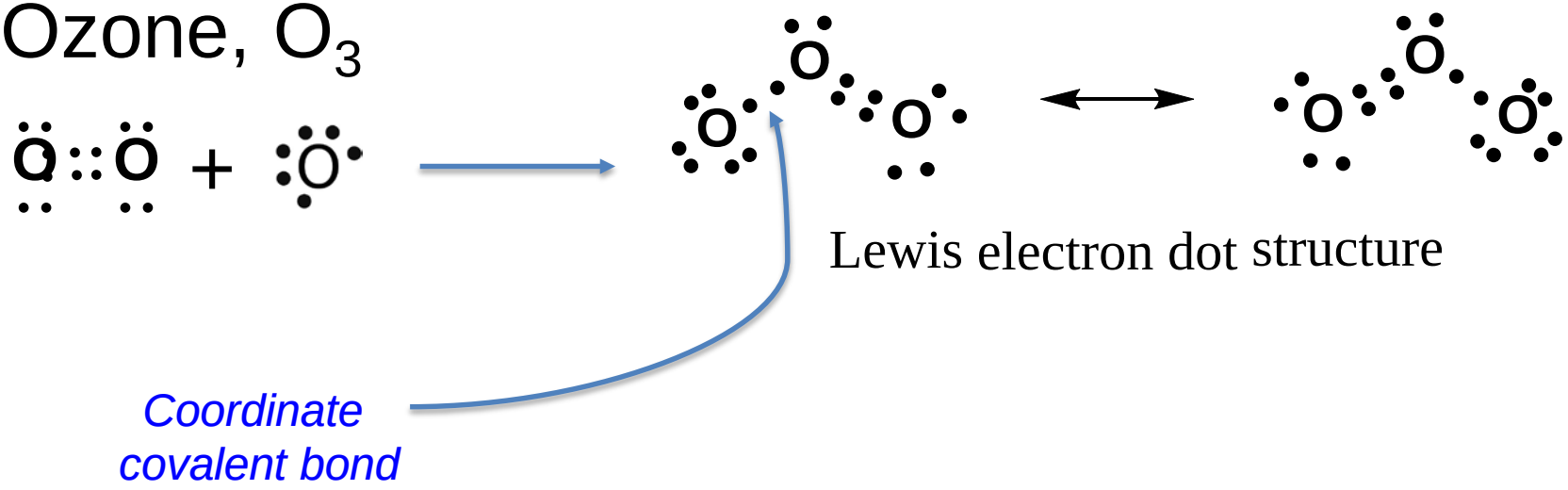
## Molecular oxygen, $O_2$

Allotropes – different forms of elements in the same state/phase

## Ozone, $O_3$



# Differences in Reactivity of Ozone and Molecular Oxygen

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**$O_2(g) \rightarrow 2O(g) \quad \Delta H = +498$ kJ/mol**

However:

**$O_3(g) \rightarrow O_2(g) + O(g) \quad \Delta H = +106$ kJ/mol**

- Ozone is much more reactive than $O_2$ due to the presence of an oxygen-oxygen single bond
- Easier for an oxygen free radical to be generated from ozone which may be damaging to biological molecules such as DNA and proteins
- Ozone is dangerous for biological organisms

# What property of $O_3$ makes it more soluble in water than $O_2$ in water? (HSC 2011)

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A. $O_3$ is a polar molecule.

B. $O_3$ has a resonance structure.

C. $O_3$ is a highly reactive molecule.

D. $O_3$ has a coordinate covalent bond.

# Ozone in Troposphere

- Formed in photochemical smog from chemical reactions between primarily exhaust gases from energy production, sunlight and oxygen
- The reactions depend on the weather, sunlight intensity and for example, motor vehicle numbers
- Ozone concentration is an accepted indicator of smog level

# Reactions in the Troposphere

$NO_2$ + sunlight $\rightarrow$ NO + O

O + $O_2$ $\rightarrow$ $O_3$ (increased ozone levels in troposphere)

NO + $O_3$ $\rightarrow$ $NO_2$ + $O_2$

<u>BUT…</u>

**NO + $O_2$ + VOCs + sunlight $\rightarrow$ $NO_2$ (lead to more $O_3$)**

**$NO_2$ + VOCs $\rightarrow$ peroxyacyl nitrates (PANs) (major irritants)**

***Q18 2009 HSC (5 marks), see p32***

***"There has been an increase in the concentration of the oxides of nitrogen in the atmosphere as a result of combustion.***
***Assess both the evidence to support this statement and the need to monitor these oxides."***

# Model Answer

CSIRO and NSW EPA take direct measurements of $NO_x$

Major sources of $NO_x$ are combustion of coal in power stations and fuel in motor vehicles.

$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$ (COMBUSTION)

$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$

$NO_2(g)$ is involved in the production of ozone, a pollutant, in the lower atmosphere in the presence of sunlight.

$NO_{2(g)} + UV \longrightarrow NO_{(g)} + O_{(g)}$

$O_{(g)} + O_{2(g)} \longrightarrow O_{3(g)}$

Catalytic converters on cars reduce the emissions of $NO_x$ by reducing $NO_x$ to $N_2$. $NO_x$ also contributes to acid rain which adversely affects both living organisms and man-made structures.

$2NO_{2(g)} + H_2O_{(l)} \longrightarrow HNO_{2(aq)} + HNO_{3(aq)}$

# Diesel Exhaust Fluid (DEF)

- To reduce the production of soot/VOCs, diesel engines are run with an excess of air, as this minimises the exhausting of partially or unburnt fuel. However, these conditions produce high levels of $NO_x$ from the $N_2$ in air

- DEF is 32% urea in water. In the presence of a suitable catalyst, the DEF is combined with the hot diesel exhaust gases to convert $NO_x$ to $N_2$

**Urea forms ammonia:**

$$(NH_2)_2CO + H_2O \rightarrow 2\ NH_3 + CO_2$$

**Ammonia reacts with NOx:**

$$2\ NO + 2\ NH_3 + 0.5\ O_2 \rightarrow 2\ N_2 + 3 H_2O$$

$$3\ NO_2 + 4\ NH_3 \rightarrow 3.5\ N_2 + 6 H_2O$$

# Ozone in the Stratosphere

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- Maximum concentration (~12 ppm) of ozone occurs at about 25 km above the earth's surface (stratosphere).

- Ozone in the stratosphere absorbs most of the solar UV-B (320-280 nm) radiation, which, if it reaches ground level, causes skin cancer, eye cataracts, severe sunburn, etc.

$$O_2 + \text{UV light} \rightarrow 2O$$

$$O + O_2 \rightarrow O_3 \quad \text{(exothermic)}$$

$$O + O_3 \rightarrow 2\,O_2 \quad \text{(exothermic)}$$

$$O_3 + \text{UV light} \rightarrow O + O_2$$

# The Ozone Hole

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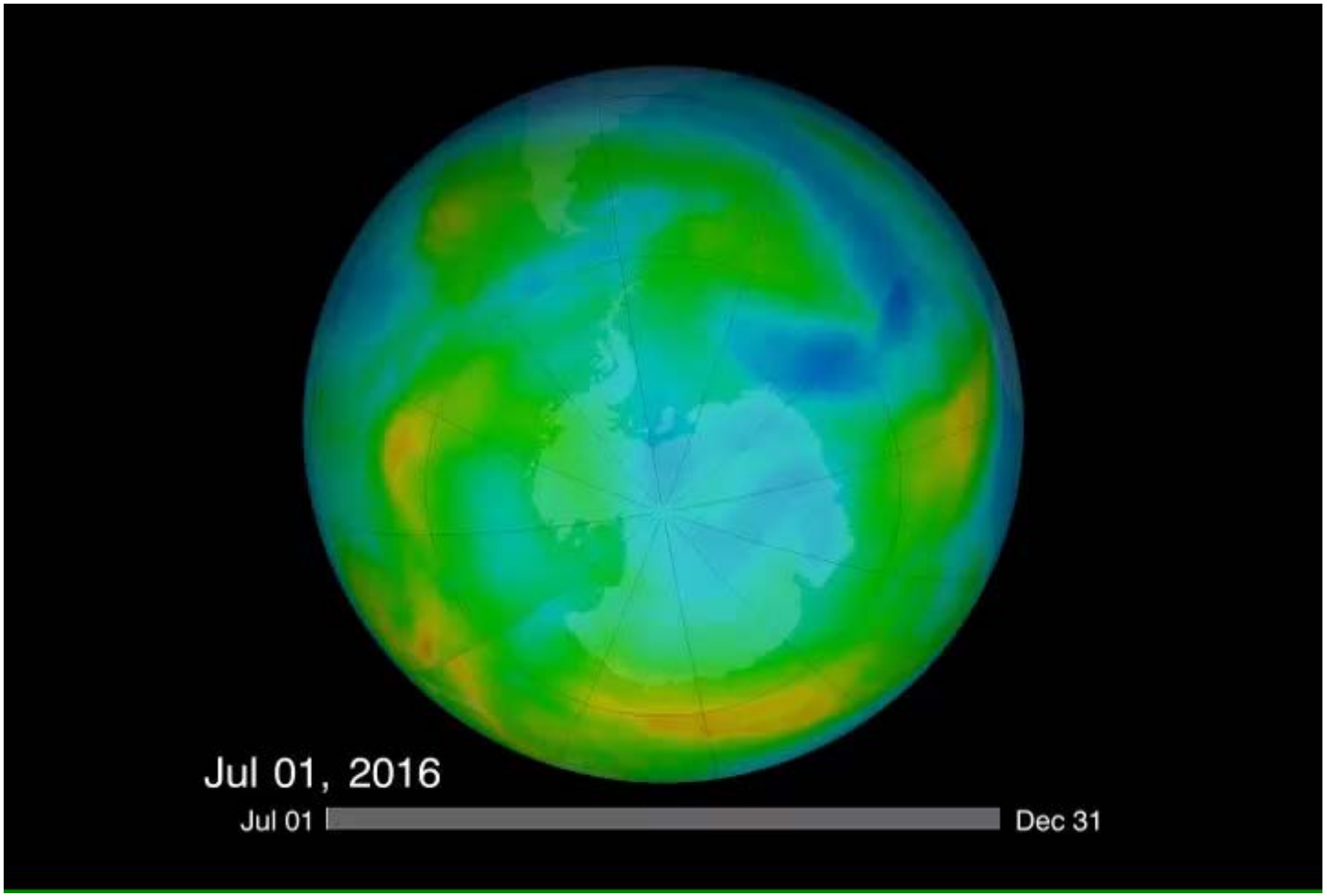
- In 1985 Dr Joe Farman (British Antarctic Survey) discovered that the concentration of ozone in the stratosphere over the Antarctic had been decreasing since the early 1970s by up to 50%
- The severe depletion of the Antarctic ozone layer occurs because of very low winter temperatures in the Antarctic stratosphere, which produce polar stratospheric clouds (PSCs)
- The 'hole' appears in spring *ie* September – October, each year
- An ozone hole has also been observed over the Arctic since the mid 1990s

# Ozone Hole over the Antarctic

https://ozonewatch.gsfc.nasa.gov/




The **purple and blue** colours are where there is the **least ozone**.

**Yellow and red** colours are where there is **more ozone**.

# Which of the following gases can cause major depletion of the ozone layer? (HSC 2011)

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A. $O_2$

B. $NO_2$

C. $CO_2$

D. $CCl_3F$

# Reactions in Stratosphere


$CCl_3F + \text{UV light} \rightarrow Cl + CCl_2F$

$Cl + O_3 \rightarrow ClO + O_2$ (ClO is very reactive)

$ClO + O \rightarrow Cl + O_2$

**Overall: $O_3 + O \rightarrow 2O_2$**

- Ozone has been converted to oxygen gas, while the Cl atom (radical) is regenerated and available for many more ozone destroying reactions.
- One Cl atom can destroy up to 100,000 ozone molecules.

**Cl is eventually removed by reactions:**

$Cl + CH_4 \rightarrow HCl + CH_3$

$ClO + NO_2 \rightarrow ClONO_2$

# What Causes the Ozone Hole?

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- CFCs are extremely stable in the troposphere and eventually find their way up to the stratosphere where they react with high energy UV light
- At the very low polar temperatures, liquid and solid PSCs form from CFCs
- Reactions on the surfaces of these PSCs significantly increase the concentration of the most reactive chlorine species, chlorine monoxide (ClO)

# *Part of the Solution*

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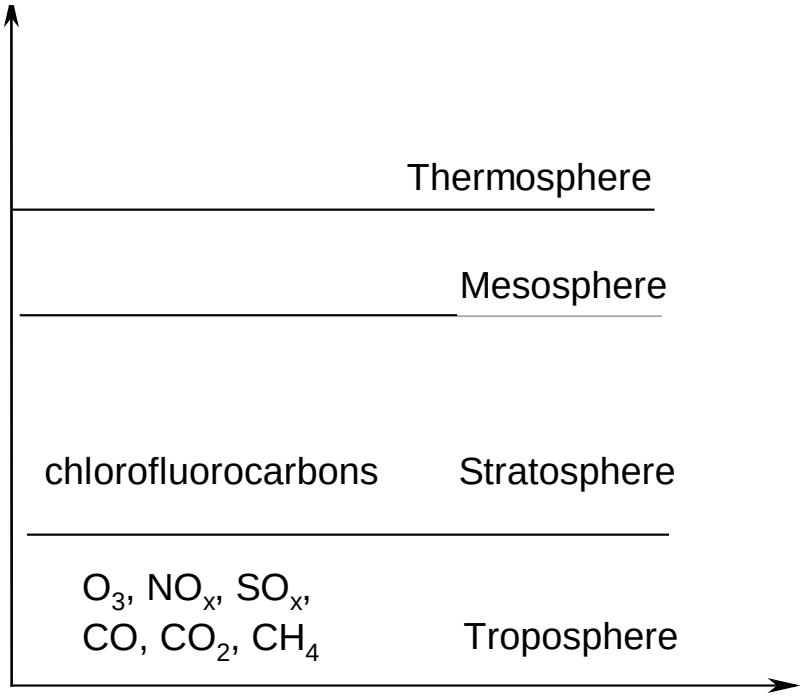
- CFCs have been replaced by hydrochlorofluorocarbons, **HCFCs** (contain H and C as well as F and Cl) and hydrofluorocarbons, **HFCs** (contain no chlorine)
- As HCFCs and HFCs contain C-H bonds that promote molecular decomposition in the troposphere
- HCFCs are now being phased out. They destroy ozone, as well as contributing to Global Warming
- HFCs have no C-Cl bonds and therefore have no ozone depleting effects. (Q27, 2004 examined this)

# Main Atmospheric Pollutants and Sources

***Q29, 2012 exam (see p32)***
***Draw a diagram to show the layered structure of the atmosphere. In your diagram include: the names of TWO atmospheric pollutants, positioned in the layers where the detrimental impact occurs and the names of the sources of the two pollutants identified.***

$O_3$ – photo-oxidation or industrial production
CO – incomplete combustion, motor vehicles, other combustion
$NO_x$ – internal combustion engine
$SO_x$ – fossil fuels combustion
$CO_2$ – fossil fuels
$CH_4$ – agriculture, anaerobic processes, LNG



# Choose the incorrect statement about ozone

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A. Ozone is a measure of pollution in troposphere.
B. Higher levels of ozone in the stratosphere are normal.
C. $O_3$ and $O_2$ are allotropes.
D. Ozone is an ionic substance.

# Past HSC Exam Questions on Chemistry and the Atmosphere

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- ***Identifying atmosphere layers*, common atmospheric pollutants and role of ozone in troposphere and stratosphere – questions on ozone structure and properties also commonly asked**

- ***Photochemical smog* – what it consists of, effects, role and source of $O_3$ and $NO_2$ (with equations)**

- ***Ozone hole* – role of CFCs (with equations), effect of HCFCs and HFCs, naming haloalkanes**

# Monitoring Water Quality

# Our Water Quality

- Water is one of our most important natural resources. Humans require clean, safe water for purposes such as: drinking, agriculture, industry and recreation

- Our water quality is at risk due to population increases, which promote urban and agricultural expansion into catchment areas

- Water needs to be monitored, managed and protected

# Our Water Quality

Water quality indicators:

- **Biological**: bacteria, algae, viruses and parasites
- **Physical**: temperature, turbidity, colour, salinity, suspended solids, dissolved solids
- **Chemica**l: pH, dissolved oxygen, biochemical oxygen demand (BOD), P and N, organic (*eg* pesticides and herbicides) and inorganic (*eg* metal ions) compounds
- **Aesthetic**: odours, colour, floating matter
- **Radioactive**: a, b and g radiation emitters

# Tests for Common Ions

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**Precipitation (gravimetric analysis)** – useful as a qualitative test for many ions and for quantitative analysis where concentrations are high *(eg)* $Ag^{+}$ to precipitate $Cl^{-}$ , $Ba^{2+}$ to precipitate $SO_4^{2-}$.

# Tests for Common Ions

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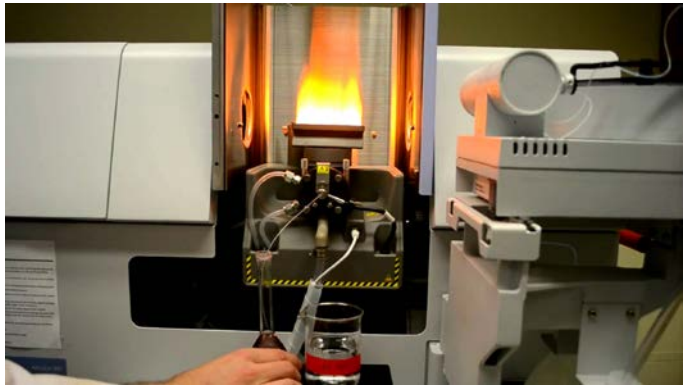
- **Atomic Absorption Spectrophotometry (AAS)** for metal ions
- AAS was developed in the 1950s by an Australian CSIRO scientist, Alan Walsh
- It uses the unique light absorption spectrum of each metal atom to measure the concentration of the metal in the water sample and is a useful method for ppm concentrations



# Tests for Common Ions

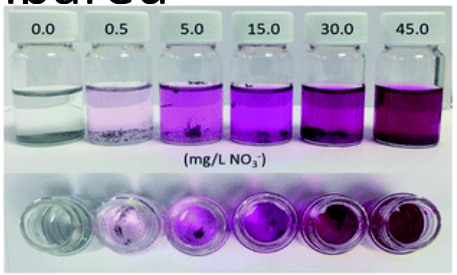
**Ion Selective Electrodes (ISEs)** for low ion concentrations *(eg)* fluoride ($F^-$), chloride ($Cl^-$), nitrate ($NO_3^-$), sulfate ($SO_4^{2-}$) ion concentrations


*Source: www.hannainst.com*

# Tests for Common Ions

**Colorimetric** – used commonly for measuring low phosphate ($PO_4^{3}$) and nitrate concentrations

- Ammonium molybdate, $(NH_4)_2MoO_4$ added to **phosphate** sample, followed by ascorbic acid (vitamin C) => intense blue colour (molybdenum blue), which can be compared to standard phosphate solutions treated identically




- **Nitrate** ($NO_3^-$) reduced to nitrite ($NO_2^-$) and then colour-producing reagent added to form pink-purple azo-dye

# Total Dissolved Solids (TDS)

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- Measurement of mass of residue by evaporation of filtered water from a known volume of water sample. Unit usually mg/L

**<500 mg/L good quality drinking water**

**>1000 mg/L poor quality**

- As the majority of the solids are typically salts (ionic), electrical conductivity of the water is often used to measure TDS. Units are in Siemens $cm^{-1}$ or mS $cm^{-1}$

# Test for Hardness

- ‘Hard’ describes water that will not lather with soap but instead forms a ‘scum’
- Soap ‘scum’ is the insoluble salt of the long chain (~C16-C18) alkanoic acid of the soap bound to a metal cation

***(eg)*** $\mathbf{Ca^{2+}(\mathit{aq}) + C_{17}H_{35}COO^{-}(\mathit{aq}) \rightarrow Ca(C_{17}H_{35}COO)_2(\mathit{s})}$

- The ion causing hardness is predominantly calcium but magnesium and aluminium also contribute

# Test for Hardness

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- Shaking a water sample with soap is a method of determining whether the water is ‘hard’ or ‘soft’. If the water is hard then a precipitate or scum will form
- Hardness is measured quantitatively by an EDTA titration in which EDTA binds to the cation ($Ca^{2+}$,$Mg^{2+}$)

| *Classification* | *ppm or mg/l* | *grains/gal* |
|---|---|---|
| Soft | 0 - 17.1 | 0 - 1 |
| Slightly hard | 17.1 - 60 | 1 - 3.5 |
| Moderately hard | 60 - 120 | 3.5 - 7.0 |
| Hard | 120 - 180 | 7.0 - 10.5 |
| Very Hard | 180 & over | 10.5 & over |

Table 1 – Hardness Classification

# HSC Past Exam Question- 5 marks

***A sample of hard water contains $6\times10^{-4}$ mol $L^{-1}$ of magnesium carbonate. Calculate the mass, in mg, of magnesium carbonate in 150 mL of this sample.***

Moles $MgCO_3$ in 150 mL = concentration x volume (L)

= 6 x $10^{-4}$ mol/L x 0.150 L

= 0.00009 mol

Mass $MgCO_3$ = mol x molar mass

= 0.00009 mol x 84.3 g/mol

= 0.007587 g

= 7.587 mg

= 8 mg (1 significant figure)

# Dissolved Oxygen and Biochemical Oxygen Demand (BOD)

- Small amounts $O_2$ gas dissolve in water (~9 ppm at 20$^{o}$C)
- Essential for aquatic life; If dissolved $O_2$ <5 ppm aquatic life suffers
- **Biochemical oxygen demand (BOD)** is a measure of the dissolved oxygen required for the complete breakdown of organic matter in a sample of water by bacteria
- In natural and unpolluted water ~5 ppm
- Raw sewage and stormwater runoff from urban areas have large BOD (100 – 500 ppm) due to higher concentrations of bacteria

# Measuring Dissolved $O_2$

**Dissolved oxygen** in water measured by:

- **Titration (Winkler method)** – dissolved $O_2$ oxidises $Mn^{2+}$ to $Mn^{4+}$ (in alkaline solution), which oxidises $I^-$ to $I_2$, which is then titrated with thiosulfate, $S_2O_3^{2-}$ in the presence of starch – forms intense blue at end point

- **Oxygen-sensitive electrode**

# N:P ratio

- N - present mainly as nitrate, nitrite, ammonia, organic N
- P - present mainly as phosphate
- Sources of N and P: fertilisers, sewage, detergents
- A **ratio of 10:1** (approximately) is recommended for N:P.

  A lower ratio indicates conditions favourable for eutrophication **(the enrichment of a water body by nutrients such as fertilisers and/or sewage)** and hence high algal growth
- Algae use nutrients, deplete oxygen – major damage

# 2010 HSC Exam Q10

**What is the consequence of having large concentrations of $Mg^{2+}$ and $Ca^{2+}$ ions in waterways?**

A. Turbidity

B. Hardness

C. Eutrophication

D. Heavy metal contamination

# Factors Affecting Levels of Ions and Other Substances in Natural Water Ways

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- Rainwater dissolves $CO_2$ (also $SO_2$ and $NO_x$) from the atmosphere, cations *eg* $Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $Cu^{2+}$, $Zn^{2+}$,and anions eg $SO_4^{2-}$, $Cl^-$, $CO_3^{2-}$, from rocks and soils

- Agricultural activities and land clearing can result in fertilisers, pesticides, herbicides and inorganic salts being added to natural water

- Industrial activities and mining – organics from petrochemical industries, also heavy metals such as Cu, Hg, Zn etc.

# Factors Affecting Levels of Ions and Other Substances in Natural Water Ways

- Sewage and stormwater runoff – microorganisms and organic substances

- Leaching from rubbish dumps and mine tailings *(eg)* Cd, Hg, Pb from batteries, Zn, nitrate, phosphate, from decaying organic waste

# Purifying and Sanitising Mass Drinking Water Supplies

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- **Catchment should be protected** with people and activity excluded from the areas immediately surrounding water storage facilities

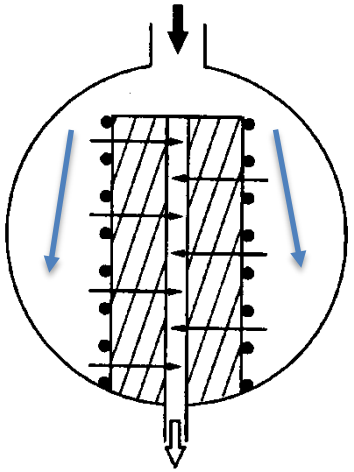
- Water is treated prior to being made available for human consumption

1. Ferric chloride (Sydney) or aluminium salts are used as a **flocculating agent** to cause small precipitate particles to come together to form large particles which can then settle out
2. Water is filtered through sand and gravel
3. Water is **chlorinated** (by hypochlorite ions, $OCl^-$) to kill bacteria and some viruses.
4. **Fluoride**, in the form of NaF, is sometimes added to strengthen tooth enamel in growing children
5. Water quality is monitored at every stage.

# Purifying and Sanitising Mass Drinking Water Supplies

- Membrane filters are widely used for filtering very small particles (> 0.2 μm) from drinking water, treated sewage and water for industry

- Dirty water in at top, clean water out the bottom



## $FeCl_3$ and $Al_2(SO_4)_3$ can be used in the purification of town water supplies. What is the role of these chemicals? (HSC 2011)

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A. To disinfect water by removing bacteria.

B. To remove particulate material by flocculation.

C. To control the concentration of total dissolved solids.

# Sample Past HSC Exam Questions and Answers

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- Questions on defining main water quality measurements and how to determine them (especially biochemical oxygen demand (BOD), hardness, P and N levels, total dissolved solids and turbidity) (2002, 2004, 2005, 2007, 2009, 2010, 2011, 2012)

- Questions on explaining quality of water in various locations very common (1998, 2005, 2008, 2011)

- Eutrophication process (2003, 2009, Q25 2012) and questions on sanitisation (2002, 2006, 2009) also turn up

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# Next:

1. **Surveys**
2. **Top Marks Education Study Skills Workshop**

***Lecture notes will be made available soon at***

***www.cbms.mq.edu.au/hsc_enrichment***