Ozone and Ozone Depleting Substances

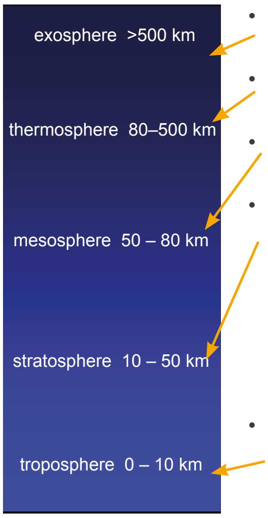
Introduction

The ***stratospheric ozone layer*** acts as an invisible shield and protects us from harmful ***ultraviolet*** (UV) radiation from the sun. Long-term exposure to high levels of ***UV-B*** can severely damage most animals, plants and microbes, so the ozone layer protects all life on Earth.

The Earth's atmosphere is 78% nitrogen (N_2) and 21% oxygen (O_2). It also contains reactive molecules and ***free radicals*** which provide most of the ***oxidising power*** of the atmosphere. These are formed almost entirely by ***photochemistry***: ozone (O_3), peroxy radicals (HO_2•, RO_2•), hydroxyl radicals (OH•) and peroxides (e.g. H_2O_2 and RO_2H).

Note: The letter '**R**' in these formulas usually stands for an organic 'radical' such as CH_3- C_2H_5- etc. The **dot** in formulas such as OH• indicates the presence of an ***unpaired electron***. Such species are known as free radicals and are generally very reactive.

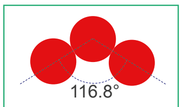
Atmospheric layers



- The "**exosphere**", above 500 km, fades into space.
- In the "**thermosphere**" (80 – 500 km) temperature increases with altitude again.
- In the "**mesosphere**" (50 – 80 km) temperature decreases with altitude.
- In the **stratosphere** temperature increases with altitude, due to the absorption of ***UV*** light by O_2 and O_3. Since warmer air lies above colder air, ***convection*** is inhibited. (99% of the atmosphere is below 40 km.) The **stratosphere** begins at a height of about 10 km but is generally lower at the poles (~7 km) and higher at the equator (15–20 km).
- The lower atmosphere or **troposphere** – the part in which weather occurs – is the lowest 10 km or so of the atmosphere.

What is ozone?

Ozone is an ***allotrope*** of oxygen which has three oxygen atoms in each molecule. It has a distinctive smell reminiscent of chlorine. Like chlorine it is chemically reactive and toxic and can be used as a ***disinfectant***. Ozone in the stratosphere protects us from most of the harmful solar UV radiation. About 10% of atmospheric ozone occurs in the troposphere, i.e. the lowest layer of the atmosphere, typically in concentrations of around 20 or 30 ***ppm*** (parts per million). Higher concentrations (e.g. 100 ppm) occur in heavily polluted areas. Ozone in the troposphere is undesirable because it increases incidence of respiratory diseases.

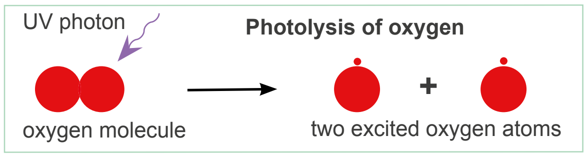


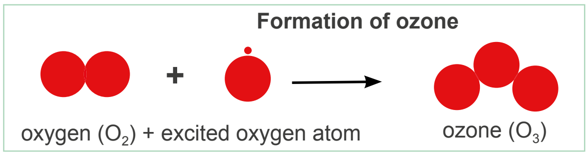
ozone (O_3)

Stratospheric ozone

- Most of the Earth's ozone (~90%) is in the lower part of the stratosphere (ca. 15 – 35 km) where it is formed from the direct ***photolysis*** of oxygen by UV with a ***maximum wavelength*** of light of 242 ***nm***.

Step 1: $O_2 + hf \rightarrow O\bullet + O\bullet$ **Step 2:** $O_2 + O\bullet \rightarrow O_3$





Here the energy of the ultraviolet ***photon*** is written as *hf*, where *h* is ***Planck's constant*** and *f* is the ***frequency*** of the radiation in hertz. The excited oxygen atoms are very reactive and typically last less than a second in the stratosphere.

- The bonds in ozone molecules are not as strong as those in oxygen molecules; they can be broken by low energy UV (320 nm).

Step 1: $O_3 + hf \rightarrow O\bullet + O_2$ **Step 2:** $O\bullet + O_3 \rightarrow 2\ O_2$

The system reaches a steady state where the rate of ozone loss equals the rate of ozone formation.

Tropospheric ozone

Tropospheric ozone is formed by a different mechanism. The minimum wavelength of light reaching the troposphere (below 17 km) is about 295 nm; this is UV, but has almost 20% less energy than 242 nm UV. So ozone formation in the troposphere is not the result of direct oxygen photolysis; it is formed indirectly by photolysis of ***nitrogen dioxide*** and other reactions.

Step 1: $NO_2 + hf \rightarrow NO + O\bullet$ **Step 2:** $O\bullet + O_2 \rightarrow O_3$

Nitrogen dioxide (NO_2) is thus an ***ozone precursor***. Others precursors include carbon monoxide (CO) and ***VOC***s (volatile organic compounds).

Destruction of the ozone layer

As mentioned above, low energy UV can break ozone molecules apart. However, certain chemical species can break not just one ozone molecule but maybe 100,000 of them before they are themselves removed from the atmosphere. They act like ***catalysts*** for the destruction of ozone. The principal ozone destroyers are: chlorine and bromine atoms, hydroxyl radicals (OH•) and nitric oxide (NO).

The general processes are summarised as follows:

Step 1: $\mathbf{X} + O_3 \rightarrow \mathbf{X}O + O_2$

Step 2: $\mathbf{X}O + O\bullet \rightarrow \mathbf{X} + O_2$

where **X** represents any of these: Cl, Br, NO or OH•

Note that in each case the 'catalyst' (Cl, Br, NO, OH•) is regenerated by the second reaction and so can go on to destroy more ozone molecules. This is why it is so destructive.

The presence of chlorine and bromine atoms in the stratosphere is very undesirable because they are so destructive of the ozone layer.

A variety of nitrogen oxides (NO_x) can be formed when substances are burned in air. The most significant ones are nitrogen dioxide (NO_2) and nitric oxide (NO).

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Stratospheric chlorine and bromine are produced by the photolysis of CFCs (chloro-fluoro-carbons) and BFCs (bromo-fluoro-carbons) that we have carelessly added to the atmosphere in the last 100 years.

Photolysis of trifluorochloro methane: $CF_3Cl + hf \rightarrow CF_3 + Cl$

Under normal conditions CFCs and BFCs are chemically inert and unreactive. CF_2Cl_2 (Dichloro difluoro methane) was used as the heat transfer substance in refrigerators (i.e. as a 'refrigerant') and CF_3Cl was used as a propellant for aerosol sprays. BFCs such as CF_3Br and CF_2BrCl were used as propellants in fire extinguishers.

In the mid-1970s, scientists became aware that the ozone layer was threatened by the accumulation of gases containing halogens (chlorine and bromine) in the atmosphere. Then, in the mid-1980s, scientists discovered a 'hole' in the ozone layer above Antarctica – the region of Earth's atmosphere with severe depletion. When the mechanism of their effect on the ozone layer was established, the production and use of these substances, known as Ozone Depleting Substances (ODS), was phased out by the 1987 Montreal Protocol.

In 2019 only limited, exempted ODS uses for specified, critical purposes are allowed, although these critical uses will also be phased out over time. The Montreal Protocol has led to significant reductions in the use (and consequent release to atmosphere) of ODS. Since then the ozone layer has begun to recover but it is expected that it will take several decades for the chlorine and bromine to be removed from the atmosphere (e.g. as HCl and HBr) in rain. Without the Montreal Protocol, large-scale depletion of the ozone layer would have occurred with major adverse consequences to human health, plant life growth and crop yields, marine life, carbon storage and damage to outdoor materials, both natural and synthetic.

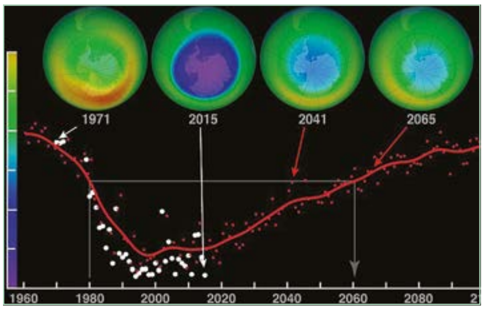

Image source: NASA

Hydroxyl radicals

Hydroxyl radicals (OH•) are highly reactive species which typically last only nanoseconds in the atmosphere. They are formed by the reaction of excited oxygen atoms with water. (These are not hydroxide ions, OH^-)

$$O\bullet + H_2O \rightarrow 2\,OH\bullet$$

Hydroxyl radicals (OH•) are **the main oxidising species in the lower atmosphere.** They react with almost every atmospheric gas other than

N_2, O_2, H_2O, CO_2 and CFCs.

The hydroxyl radical is sometimes referred to as the "detergent" of the troposphere. The rate of reaction with the hydroxyl radical often determines how long many pollutants last in the atmosphere, if they do not undergo photolysis or are not removed by rain. Pollutants, such as larger hydrocarbons, can have very short average lifetimes of less than a few hours. However, methane reacts relatively slowly with hydroxyl radicals and has an average lifetime of more than 5 years. Many CFCs have lifetimes of 50 years or more.

The **Environmental Protection Agency (EPA)** is responsible for protecting and improving the environment as a valuable asset for the people of Ireland. We are committed to protecting people and the environment from the harmful effects of radiation and pollution.

The work of the EPA can be divided into three main areas:

Regulation: EPA implements effective regulation and environmental compliance systems to deliver good environmental outcomes and target those who don't comply.

Knowledge: EPA provides high quality, targeted and timely environmental data, information and assessment to inform decision making at all levels.

Advocacy: EPA works with others to advocate for a clean, productive and well protected environment and for sustainable environmental behaviour.

Responsibilities

- Licensing of activities so that they do not endanger human health or harm the environment (e.g. waste facilities, large scale manufacturing, power plants, intensive agriculture, ionising radiation)
- Conducting inspection and enforcing regulations (e.g. public supplies of drinking water, waste management).
- Water management (e.g. monitoring and reporting on the quality of rivers, lakes, bathing water, etc.)
- Monitoring, analysing and reporting on the environment (monitoring air quality, implementing relevant EU directives)
- Regulating Ireland's greenhouse gas emissions
- Regulating ozone-depleting substances
- Environmental research and development
- Strategic environmental assessment (e.g. assessing the impact of proposed major developments).
- Radiological protection
- Guidance, accessible information and education
- Awareness raising and behavioural change (e.g. influencing positive behavioural change relating to the environment, promoting radon testing in homes and workplaces)

For more information on ozone monitoring by EPA go to:
https://www.epa.ie/air/quality/reports/ozone/

You can find out more about the work of **EPA** at **www.epa.ie**

Find this and other lessons on www.sta.ie

science & technology in action
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Ozone and Ozone Depleting Substances

Syllabus References

The main syllabus references for the lesson are:

Leaving Certificate Chemistry

Atmospheric Chemistry (p. 30)

- The ozone layer. Chlorofluorocarbons and the ozone layer. Formation of ozone in the stratosphere.
- Beneficial effect of the ozone layer.
- CFCs and HCFCs. Uses of CFCs. CFCs are believed to be the main cause of damage to the ozone layer. Effects of damage to the ozone layer.

Leaving Certificate Physics

Electromagnetic spectrum (p. 15)

- Relative positions of radiations in terms of wavelength and frequency.
- Detection of UV and IR radiation.
- Ultraviolet and ozone layer.

Science and Technology in Action is also widely used by **Transition Year** classes.

Learning Outcomes

On completion of this lesson, students should be able to:

- Distinguish between the different layers in the atmosphere and outline its composition
- Outline the different mechanisms by which ozone is formed in the stratosphere and in the troposphere
- Describe the role of photolysis in the formation of ozone
- Outline the main mechanisms by which the ozone layer can be damaged, especially the role of CFCs and nitric oxide
- Outline how hydroxyl radicals affect the atmosphere.

General Learning Points

These are additional relevant points which are used to extend knowledge and facilitate discussion.

- Four gases make up 99.99% of the atmosphere but many minor constituents can have an adverse effect.
- Ozone is formed in the stratosphere by direct photolysis of molecular oxygen.
- Ozone is formed in the troposphere by photolysis of NO_2 which releases excited oxygen atoms.
- The destruction of the ozone layer (stratospheric ozone) is catalysed by chlorine and bromine atoms, hydroxyl radicals (OH•) and nitric oxide (NO).
- Photolysis of CFCs releases reactive chlorine atoms.

Student Activities

1. Make a poster to show the different layers in the atmosphere.
2. Make a computer presentation or animation to show how ozone is formed and destroyed in the stratosphere. What are the beneficial effects of the ozone layer?
3. Make a computer presentation or animation to show how ozone is formed and destroyed in the troposphere.
4. The part of the spectrum immediately beyond the violet, between 200 and 400 nm, is the ultraviolet light (UV). It is usually divided into three components, with increasing energy:
   - UV-C: 200-280 nm (far UV)
   - UV-B: 280-320 nm (middle UV)
   - UV-A: 320-400 nm (near UV)

   Which has the highest energy?
   Which has a damaging effect on the skin?
   Which is involved in the formation of the ozone layer?

   Summarise your results as slides or as a poster.
5. For each of the main oxides of nitrogen (NO, NO_2, N_2O) in the atmosphere investigate
   - its main sources
   - its effect (if any) on ozone levels
   - how it is removed from the atmosphere
6. Nitrous oxide (N_2O) is not very reactive under ordinary conditions. Investigate how N_2O can act as a carrier of reactive nitrogen to the stratosphere.

True/False Questions

a)	Nitrogen is the most abundant gas in the atmosphere.	T F
b)	Molecules containing unpaired electrons are know as free radicals and are chemically very reactive.	T F
c)	The lowest layer of the atmosphere is the stratosphere.	T F
d)	Ozone is formed by different mechanisms in different parts of the atmosphere.	T F
e)	Stratospheric ozone absorbs harmful solar UV rays.	T F
f)	Chlorine and bromine atoms act as catalysts for the destruction of stratospheric ozone.	T F
g)	Under normal conditions CFCs (chloro-fluoro-carbons) are chemically very reactive.	T F
h)	Hydroxyl radicals are the main oxidising species in the lower atmosphere.	T F
i)	Nitrogen dioxide, carbon monoxide and volatile organic compounds are ozone precursors.	T F

Check your answers to these questions on www.sta.ie.

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Examination Questions

Leaving Certificate Chemistry (HL) 2016, Q. 11 c

Environmental scientists continue to be concerned about the slow recovery of ozone concentrations in the stratosphere despite the successes of the 1987 Montreal Protocol, an international treaty designed to control substances that deplete ozone.

(i) What is the beneficial effect of the ozone layer?

(ii) How is ozone formed in the stratosphere?

(iii) CFCs release chlorine radicals when they photodissociate in the stratosphere. Describe using balanced equations why chlorine radicals are so damaging to the ozone layer.

Leaving Certificate Chemistry (OL) 2011, Q. 11 b

Outline the chemical processes that give rise to the occurrence of ozone gas in the stratosphere. Why is ozone gas not produced in this way in the lower atmosphere?

The destruction of the ozone layer is a matter of environmental concern. A non-metal oxide and chlorine atoms from CFCs are considered to be mainly responsible for the destruction of ozone.

(i) What are CFC molecules?

(ii) Why do CFC molecules have long residence times in the lower atmosphere?

(iii) Give a major use of CFCs before their production was restricted in 1987.

(iv) Name the non-metallic oxide that is associated with ozone destruction in the stratosphere. Give a source of this oxide.

Leaving Certificate Chemistry (OL) 2013, Q. 11 c

Oxygen (O_2) and ozone (O_3) are forms of the same element. Because of concern about damage to the Earth's ozone layer by CFCs, these compounds have been banned and have been replaced by other substances e.g. HCFCs.

(i) Give a brief outline of the extraction of oxygen (O2) from air.

(ii) What do the letters CFC and HCFC represent? Give one common use that was made of CFCs before they were banned.

(iii) What is the importance of the ozone layer?

Leaving Certificate Chemistry (OL) 2015, Q. 11 c

(i) Oxygen gas (O_2) is produced industrially by liquefaction and fractional distillation of air. What other gas is the major product of this process? What is the approximate percentage of this second gas in the atmosphere? Give a widespread use for this second gas.

(ii) Name the other form of oxygen gas (O_3) formed in the stratosphere. What environmentally beneficial effect does O_3 have? Identify a group of chemicals that damages O_3.

Leaving Certificate Physics (HL) 2008, Q. 11 g

High-energy radiation of frequency 3.3×10^{14} Hz is used in medicine. What is the energy of a photon of this radiation?

(Planck constant = 6.6×10^{-34} J s; speed of light = 3.0×10^{8} m s^{-1})

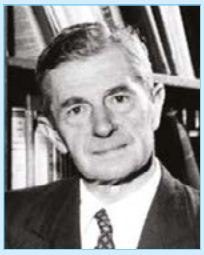
Did You Know?

Importance of nitrogen

- Nitrogen is an essential component of DNA, RNA, and amino acids. Nitrogen gas in the atmosphere is unavailable for use by most organisms because the strong triple bond between the N atoms in N_2 molecules makes it relatively inert.
- The N_2 gas must first be converted to a more chemically available form such as ammonium (NH^{4+}), nitrate (NO^{3-}), or organic nitrogen [e.g. urea, $(NH_2)_2CO$].
- The rather inert nature of N_2 means that biologically available nitrogen is often in short supply in natural ecosystems, limiting plant growth, even though it is the most abundant component of the atmosphere.
- Nitrogen and oxides of nitrogen can be released from the soil by various bacteria. NO and NO_2 are also formed by combustion in air and by lightning and they contribute to ozone destruction.

Biographical Notes

Sydney Chapman (1888 – 1970)



When he was 16 Sydney Chapman, from Salford, England, won a scholarship to study at Manchester in 1904. He completed an engineering degree but then studied mathematics in Cambridge and graduated in first place. From 1910 to 1914 he worked in the Royal Greenwich Observatory. He later lectured in Cambridge and Oxford in mathematics.

In the 1930s he worked out the photochemical processes that give rise to the ozone layer. He was one of the pioneers of solar-terrestrial physics. He studied magnetic storms and aurorae and explained how they involved the interaction between the Earth's magnetic field and the solar wind.

On retirement in 1953 he taught and conducted research in many countries around the world. He received numerous awards for his work in mathematics and high altitude atmospheric phenomena.

Revise The Terms

Can you recall the meaning of the following terms?
Revising terminology is a powerful aid to recall and retention.

allotrope, catalyst, convection, disinfectant, free radical, frequency, hydroxyl radical, maximum wavelength, nitrogen dioxide, nm, oxidising power, ozone precursor, photochemistry, photolysis, photon, Planck's constant, ppm, stratosphere, troposphere, unpaired electron, UV, UV-B, VOCs.

Check the Glossary of terms for this lesson on www.sta.ie