

Wednesday 16 January 2013 – Morning

AS GCE CHEMISTRY B (SALTERS)

F332/01/TEST Chemistry of Natural Resources

Candidates answer on the Question Paper.

OCR supplied materials:

- *Data Sheet for Chemistry B (Salters)* (inserted)
- *Advance Notice: 'A hole in the sky'* (inserted)

Other materials required:

- Scientific calculator

Duration: 1 hour 45 minutes



Candidate
forename

Candidate
surname


Centre number

Candidate number

INSTRUCTIONS TO CANDIDATES

- The Inserts will be found in the centre of this document.
- Write your name, centre number and candidate number in the boxes above. Please write clearly and in capital letters.
- Use black ink. HB pencil may be used for graphs and diagrams only.
- Read each question carefully. Make sure you know what you have to do before starting your answer.
- Write your answer to each question in the space provided. If additional space is required, you should use the lined pages at the end of this booklet. The question number(s) must be clearly shown.
- Answer **all** the questions.
- Do **not** write in the bar codes.

INFORMATION FOR CANDIDATES

- The number of marks is given in brackets [] at the end of each question or part question.
-  Where you see this icon you will be awarded marks for the quality of written communication in your answer.
- This means for example you should:
 - ensure that text is legible and that spelling, punctuation and grammar are accurate so that meaning is clear;
 - organise information clearly and coherently, using specialist vocabulary when appropriate.
- You may use a scientific calculator.
- The insert '*A hole in the sky*' is provided for use with question 5.
- A copy of the *Data Sheet for Chemistry B (Salters)* is provided as an insert with this question paper.
- You are advised to show all the steps in any calculations.
- The total number of marks for this paper is **100**.
- This document consists of **20** pages. Any blank pages are indicated.



Answer **all** the questions.

- 1 Many seashells contain calcium carbonate. The carbonate ions, CO_3^{2-} , come from atmospheric carbon dioxide that dissolves in the sea water.

(a) (i) Name **two** industrial processes that are major sources of atmospheric carbon dioxide.

.....
..... [2]

(ii) Companies use various methods for the disposal of the carbon dioxide they produce to prevent its release straight into the atmosphere.

Suggest **two** methods that they could use for disposal of carbon dioxide.

.....
.....
..... [2]

(b) Carbon dioxide is a gas at room temperature. Silicon dioxide, another Group 4 oxide, is a solid with a high melting point.

Explain this difference in melting point in terms of bonding and structure.

.....
.....
.....
.....
.....
.....
..... [3]

(c) Carbon dioxide acts as a greenhouse gas because it can absorb infrared radiation.

(i) Describe what happens to carbon dioxide molecules when they absorb the infrared radiation.

.....
..... [1]

- (ii) The changes that happen after the process in (c)(i) result in the warming of the troposphere.

Describe these changes and explain how they warm the troposphere.

.....

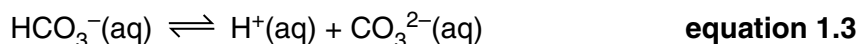
 [2]

- (d) In an air sample that was analysed, carbon dioxide was found to be present at a concentration by volume of 395 parts per million.

Calculate the percentage of carbon dioxide in the sample.

% carbon dioxide = [1]

- (e) When carbon dioxide dissolves in water, the following reactions occur.



- (i) Give the systematic name of the HCO_3^- ion.

..... [1]

- (ii) The reaction in **equation 1.3** can reach a state of dynamic equilibrium.

Explain what is meant by the term *dynamic equilibrium*.

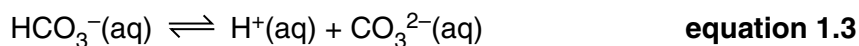
.....

 [2]

- (iii) Suggest why the balance of $\text{CO}_2(\text{g})$ in the atmosphere and $\text{CO}_2(\text{aq})$ in the oceans cannot be regarded as a dynamic equilibrium.

.....

 [1]



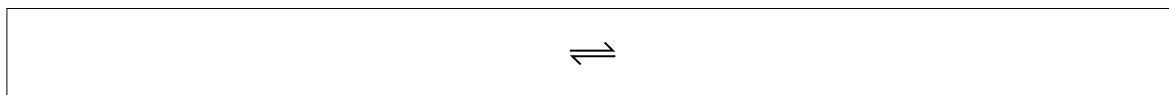
- (iv) The concentration of hydrogen ions in a sample of sea water is increased.

Using **equation 1.3**, describe and explain what would happen, if anything, to the concentration of carbonate ions.

.....

 [2]

- (v) Give the overall equation for the reaction of gaseous carbon dioxide with water that produces CO_3^{2-} ions.



[1]

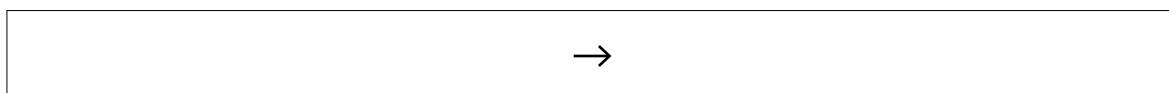
- (f) Mineral water often contains dissolved carbon dioxide. The water also contains a range of dissolved ionic compounds.

A student analyses a sample of mineral water to check the amount of dissolved sulfate ions, SO_4^{2-} , it contains.

- (i) The student adds barium chloride solution to the water to precipitate out the sulfate ions as barium sulfate. The student collects, dries and weighs the precipitate.

Write the **ionic** equation for the precipitation of barium sulfate.

Include state symbols.



[2]

- (ii) From the results, the student calculates that the mineral water contains sulfate ions at a concentration of $7.4 \times 10^{-5} \text{ mol dm}^{-3}$. The student looks at the label on the bottle and finds that the concentration is quoted in g dm^{-3} .

Calculate the concentration of sulfate ions in the water in g dm^{-3} .

Give your answer to **two** significant figures.

concentration of sulfate ions = g dm^{-3} [3]

- (iii) Suggest why the presence of CO_3^{2-} ions in the mineral water might lead to the student obtaining a higher value for the sulfate ion concentration than is given on the label on the bottle.

.....
.....
..... [1]

[Total: 24]

- 2 Leafcutter ants are responsible for producing some of the halogenoalkanes that are released into the Earth's atmosphere. The ants have been found to be responsible for producing large quantities of chloromethane and bromomethane.

Halogenoalkane	Estimated global emissions / tonnes per year	Atmospheric lifetime / years
Chloromethane, CH_3Cl	800	1.3
Bromomethane, CH_3Br	500	0.7

- (a) Why does chloromethane not photodissociate in the troposphere?

.....

 [1]

- (b) If a bromomethane molecule reaches the stratosphere, UV radiation breaks the C–Br bond in the molecule, forming bromine atoms.

- (i) The C–Br bond has an enthalpy of $+290 \text{ kJ mol}^{-1}$.

Calculate the minimum energy (in Joules) needed to break a **single** C–Br bond.

Avogadro constant, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$

minimum energy = J [2]

- (ii) Calculate the frequency of radiation that is needed to break a **single** C–Br bond.

Planck constant, $h = 6.63 \times 10^{-34} \text{ J Hz}^{-1}$

frequency = Hz [2]

(c) Chloromethane and bromomethane are both gases at room temperature whilst water is a liquid.

(i) Name **both** types of intermolecular bond that can form between molecules of chloromethane.

.....
..... [2]

(ii) Water molecules are held together by hydrogen bonds.

Draw a diagram to show how **two** water molecules can be linked by a hydrogen bond.

Include relevant lone pairs and partial charges in your diagram.

[4]

(iii) Hydrogen bonds only form when hydrogen atoms are bonded to atoms of certain elements.

Name these elements.

.....
..... [1]

- (d) The following table gives values for the boiling points of bromomethane, chloromethane and water:

	Boiling point/K
Bromomethane	277
Chloromethane	249
Water	373

Use ideas about intermolecular bonds to explain:

- (i) why chloromethane has a lower boiling point than water;

.....
 [1]

- (ii) why bromomethane has a higher boiling point than chloromethane.

.....

 [2]

- (e) Most of the chloromethane and bromomethane molecules that enter the troposphere are removed by reaction with hydroxyl radicals.

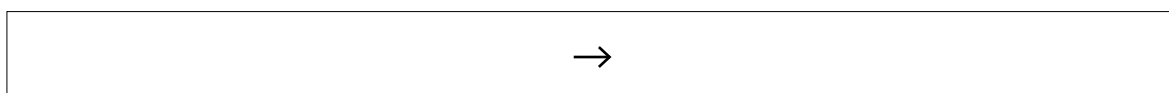
Draw a 'dot-and-cross' diagram for the hydroxyl, OH, radical.

Show outer shell electrons only.

[1]

- (f) The chloromethane and bromomethane that dissolve in the oceans are hydrolysed by the water, releasing HCl or HBr.

- (i) Write the equation for this hydrolysis of chloromethane.



[1]

(ii) Name the organic compound that forms in the reaction in (f)(i).

..... [1]

(iii) Underline **two** of the following words to describe the hydrolysis reaction in (f)(i).

addition electrophilic elimination nucleophilic radical substitution

[2]

(g) The rates of hydrolysis of chloromethane and bromomethane may depend on either of the factors shown below:

- the polarity of the carbon–halogen bond
- the strength of the carbon–halogen bond.

(i) State which bond, C–Cl or C–Br, is more polar and explain why.



In your answer, you should use technical terms, spelled correctly.

.....

 [1]

(ii) Suggest which bond, C–Cl or C–Br, is stronger and explain why.

.....

 [1]

(iii) Under the same reaction conditions, the hydrolysis of bromomethane occurs more rapidly than the hydrolysis of chloromethane.

Explain why this observation indicates that bond strength contributes more than bond polarity to the rate of hydrolysis.

.....

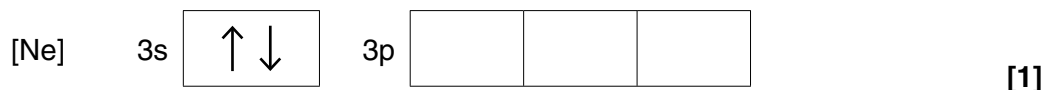
 [1]

[Total: 23]

- 3 Wine labels often show that the wine contains sulfites, because sulfur dioxide gas has been added as a preservative. Strict legal limits have been placed on the amount of SO_2 that can be added to wine, because above a certain value the sulfur dioxide affects the taste of the wine.

(a) Sulfur dioxide can be made industrially by burning sulfur in air.

(i) Complete this diagram to show the arrangement of electrons in a sulfur atom.



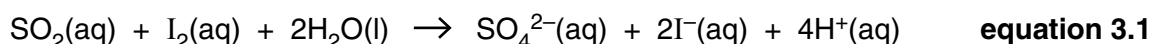
(ii) Industries producing sulfur dioxide have to make sure they do **not** allow the sulfur dioxide to escape into the atmosphere.

Name a type of pollution caused by sulfur dioxide in the atmosphere.

..... [1]

(b) The concentration of sulfur dioxide in a sample of white wine can be found by titrating the wine with a solution of iodine.

The equation for the reaction between sulfur dioxide and iodine is shown below.



(i) Give the oxidation states of the iodine and sulfur before and after the reaction.

Oxidation state of sulfur in:

SO_2 SO_4^{2-}

Oxidation state of iodine in:

I_2 I^- [2]

(ii) Give the reducing agent in the reaction shown in **equation 3.1**.

Explain your answer in terms of oxidation states.

reducing agent:

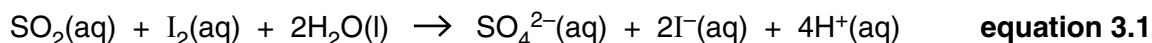
explanation:

..... [2]

(iii) Give the colour and physical state of the iodine that would be used to make the iodine solution.

..... [1]

- (c) A sample of white wine is analysed for its sulfur dioxide content by titrating it with an aqueous solution of iodine.



- (i) Name a suitable piece of equipment for adding the aqueous iodine solution to the wine.
 [1]
- (ii) 15.80 cm^3 of $0.0100\text{ mol dm}^{-3}$ aqueous I_2 solution is needed to react with 50.00 cm^3 of the wine.

Calculate the number of moles of iodine, I_2 , used in the titration.

moles I_2 = mol [1]

- (iii) Use your answer to (ii) and **equation 3.1** to write down the number of moles of sulfur dioxide in the 50.00 cm^3 of wine.

moles sulfur dioxide = mol [1]

- (iv) What is the concentration of sulfur dioxide in the wine in mol dm^{-3} ?

concentration = mol dm^{-3} [1]

- (v) In Britain, the maximum amount of sulfur dioxide that can be added to white wine is $3.28 \times 10^{-3}\text{ mol dm}^{-3}$. Above this limit, the taste of the wine is affected.

A concentration of less than $1.56 \times 10^{-4}\text{ mol dm}^{-3}$ is insufficient to preserve the wine.

Use this information to comment on your answer to (iv).

.....
 [1]

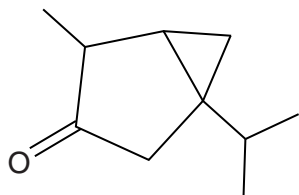
- (d) The concentration of sulfur dioxide in wine can also be found by converting the sulfur dioxide to sulfuric acid. The sulfuric acid is then titrated with sodium hydroxide solution.

How would you know when the end-point of the titration of sulfuric acid with sodium hydroxide has been reached?

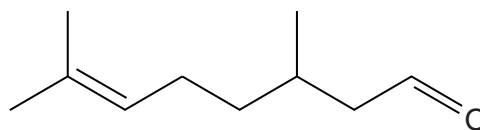
.....
 [1]

[Total: 14]

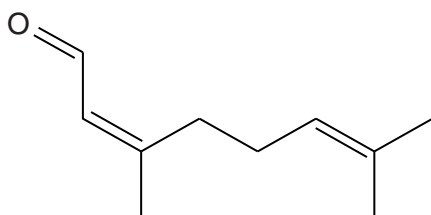
- 4 Absinthe was a popular alcoholic drink in the nineteenth century. It contained a mixture of organic compounds, including thujone, citronellal, neral and linalool. It was claimed that absinthe caused hallucinations because of the thujone it contained.



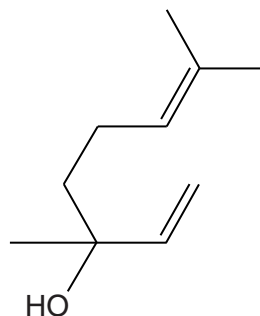
thujone



citronellal



neral



linalool

- (a) (i) Name a functional group that is present in thujone but **not** in neral.

..... [1]

- (ii) Name a functional group that is present in all these compounds **except** thujone.

..... [1]

- (b) The aldehyde group in citronellal can be oxidised by acidified dichromate(VI).

- (i) Draw the full structural formula of the functional group that forms and name this functional group.

name of functional group: [2]

- (ii) Put a tick in the table for each of the other compounds in absinthe that would be oxidised by acidified dichromate(VI).

	Linalool	Neral	Thujone
Will be oxidised			

[1]

(c) Neral has *E/Z* isomers, but linalool does not.

- (i) The diagram of neral shown on page 12 is the *Z* isomer. Draw a diagram of the *E* isomer of neral.

[1]

- (ii) Explain why neral has *E/Z* isomers.

.....

.....

.....

..... [2]

- (d) Citronellal molecules can take part in an addition polymerisation reaction.

Underline the compound from the list that **cannot** form an addition polymer.

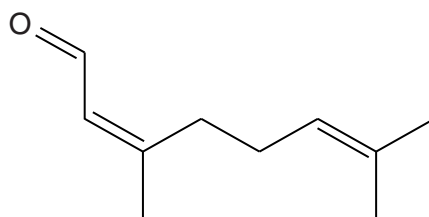
linalool

neral

thujone

[1]

14



neral

(e) Neral reacts with H_2O .

- (i) Give the reaction conditions that would be needed for the reaction of neral with H_2O , using a phosphoric acid catalyst.

.....
..... [1]

- (ii) Four organic products could form from the **complete** reaction of neral with H_2O . Assume that the aldehyde group does not react.

Draw the structures of the **four** isomeric products that could form.

[4]

CC(C)=CCCCC=CC

(f) Neral and citronellal both react with bromine. A student adds bromine water drop by drop to 1 cm³ of neral in a test-tube. The tube is shaken after each addition. The addition of bromine water is continued until no further change occurs.

Describe and explain the **similarities** and **differences** the student would observe in the two experiments.



In your answer, you should make it clear how the structures of the molecules being reacted with bromine link to the similarities and differences you have described.

..... [5]

Turn over

- 5 This question is based on the Advance Notice article '**A hole in the sky**' that is provided as an insert to this paper.

(a) Catalytic cycles include reactions that are classified as propagation reactions.

Explain what is meant by a *propagation reaction*.

Give the number of a reaction from the article that is an example of a propagation reaction.

propagation reaction

.....

reaction number

[2]

(b) **Fig. 1** in the article shows a '*dot-and-cross*' diagram that could be used to represent the bonding in a molecule of ozone.

(i) In an ozone molecule, **both** bonds have a length of 0.128 nm.

Explain why the bond length values in ozone suggest that the diagram in **Fig. 1** of the article does **not** represent the actual bonding for an ozone molecule.

.....

.....

.....

..... [2]

(ii) Explain why the diagram in **Fig. 1** indicates that the ozone molecule is V-shaped.

.....

.....

.....

..... [2]

(c) **Reactions 1** and **2** in the article result in the formation of ozone in the atmosphere.

(i) Explain why **reaction 1** occurs at a faster rate at a higher altitude.

.....

.....

.....

..... [2]

- (ii) **Reaction 2**, like most gaseous reactions, gets faster as the pressure increases.

Explain, in terms of the collision theory, why increased pressure increases the rate of a gaseous reaction.

.....

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.....

..... [2]

- (iii) **Fig. 2** in the article shows the variation of ozone concentration with altitude in the Earth's atmosphere.

Explain why the ozone concentration is highest at an altitude of around 25 km.

.....

.....

.....

..... [1]

- (d) The article tells us that the ozone in the stratosphere is beneficial because it prevents some of the UV light from the Sun from reaching the Earth's surface.

Explain why this is considered to be beneficial to humans.

.....

.....

..... [2]

Question 5 continues on page 18

- a description of the reactions by which chlorine radicals are produced from ClO radicals at 20 km altitude
- an explanation of why these chlorine radicals are **not** removed by termination reactions at 20 km altitude in the polar spring
- an explanation of how all the ozone is removed by chlorine radicals at 20 km altitude in the polar spring.

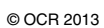


In your answer you should make it clear how the points you make link together.

..... [7]

END OF QUESTION PAPER

[illegible]



**For issue on or after:
17 NOVEMBER 2012**

AS GCE CHEMISTRY B (SALTERS)

F332/01 Chemistry of Natural Resources

ADVANCE NOTICE

**Wednesday 16 January 2013
Morning**

Duration: 1 hour 45 minutes



NOTES FOR GUIDANCE (CANDIDATES)

- 1** This leaflet contains an article which is needed in preparation for a question in the externally assessed examination F332.
- 2** You will need to read the article carefully and also have covered the learning outcomes for Unit F332 (*Chemistry of Natural Resources*). The examination paper will contain questions on the article. You will be expected to apply your knowledge and understanding of the work covered in Unit F332 to answer these questions. There are 20 marks available on the paper for these questions.
- 3** You can seek advice from your teacher about the content of the article and you can discuss it with others in your class. You may also investigate the topic yourself using any resources available to you.
- 4** For the examination on 16 January 2013 you will be given a fresh copy of this article, together with a question paper. You will **not** be able to bring your copy of the article, or other materials, into the examination.
- 5** You will not have time to read this article for the first time in the examination if you are to complete the examination paper within the specified time. However, you should refer to the article when answering the questions.

This document consists of **8** pages. Any blank pages are indicated.

INSTRUCTION TO EXAMS OFFICER/INVIGILATOR

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A hole in the sky

By Dudley Shallcross and Tim Harrison, from 'Science in School' magazine, Issue 17 (Winter 2010).

Discovering the hole

It was a serendipitous find, as Jonathan Shanklin, one of the hole's discoverers, remembers: having joined the British Antarctic Survey in 1977, he was supposed to digitise their backlog of ozone measurements – until then, handwritten data sheets. As it turned out, this included the crucial decade, the 1970s, when ozone levels began to drop.

Ozone in the stratosphere

Ozone (O_3) is a much less stable triatomic form of oxygen (O_2).

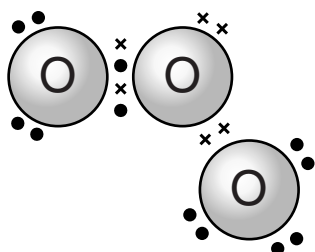


Fig. 1: 'Dot-and-cross' diagram for the bonding in ozone.

It is a pale blue gas present at low concentrations throughout the atmosphere (around 0.375 ppm for O_3 , compared to 21% for O_2) – and a double-edged sword: in the troposphere, ozone is an air pollutant which can damage the respiratory systems of humans and other animals and burn sensitive plants. The ozone in the stratosphere, however, is beneficial, preventing most of the harmful ultraviolet (UV) light emitted by the Sun from reaching Earth's surface.

The rate of ozone formation reaches a maximum in the stratosphere, the layer of Earth's atmosphere at about 10–50 km altitude, through a photochemical mechanism.

An oxygen molecule (O_2) absorbs a photon of UV light ($h\nu$) with a wavelength around 200 nm and dissociates into two oxygen atoms ($O\bullet$) (reaction 1). Each of these can then combine with another oxygen molecule to form ozone, if the pressure is high enough (approximately one thousandth of an atmosphere) to stabilise the newly formed ozone molecule (reaction 2). The higher the altitude, the faster the rate of reaction 1. The rate of reaction 2, however, is faster closer to the ground, where atmospheric

pressure is higher. As a result, the maximum amount of ozone is created at about 25 km altitude (see Fig. 2).

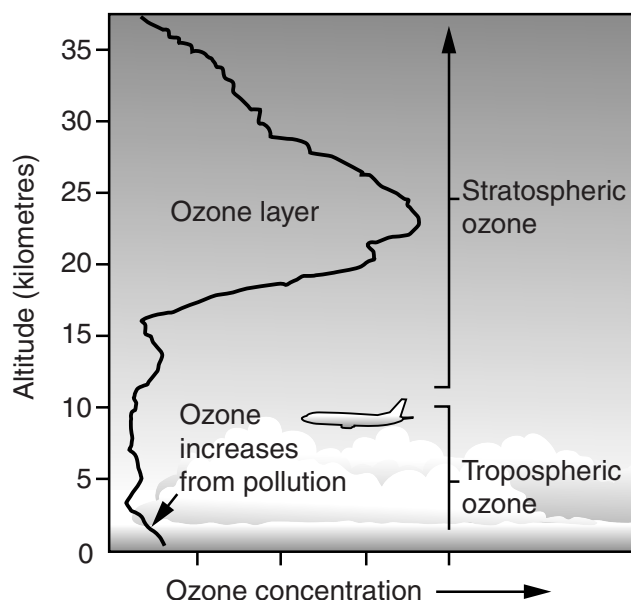


Fig. 2: Most ozone is in the stratosphere. Near Earth's surface, ozone levels increase due to pollution from human activities.

Public domain image; image source: Wikimedia Commons

The stratosphere has two important consequences for life on Earth. First, ozone itself absorbs high-energy UV radiation at around 250 nm and splits to form an oxygen radical and an oxygen molecule (reaction 3).

Between them, oxygen (reaction 1) and ozone (reaction 3) filter out of the atmosphere most of the short-wave UV radiation between 200 and 300 nm, which would otherwise be very damaging to life on Earth.

Second, reaction 3 produces a lot of heat, so the stratosphere is a warmer layer than the top of the troposphere, making the weather in the troposphere less extreme than it would otherwise be.

Reactions 2 and 3 rapidly interconvert oxygen atoms and ozone. There is another slow reaction, though, which is known to destroy both oxygen atoms and ozone, namely the reaction between these two species (reaction 4).

Reactions 1–4 are summarised in Fig. 3.

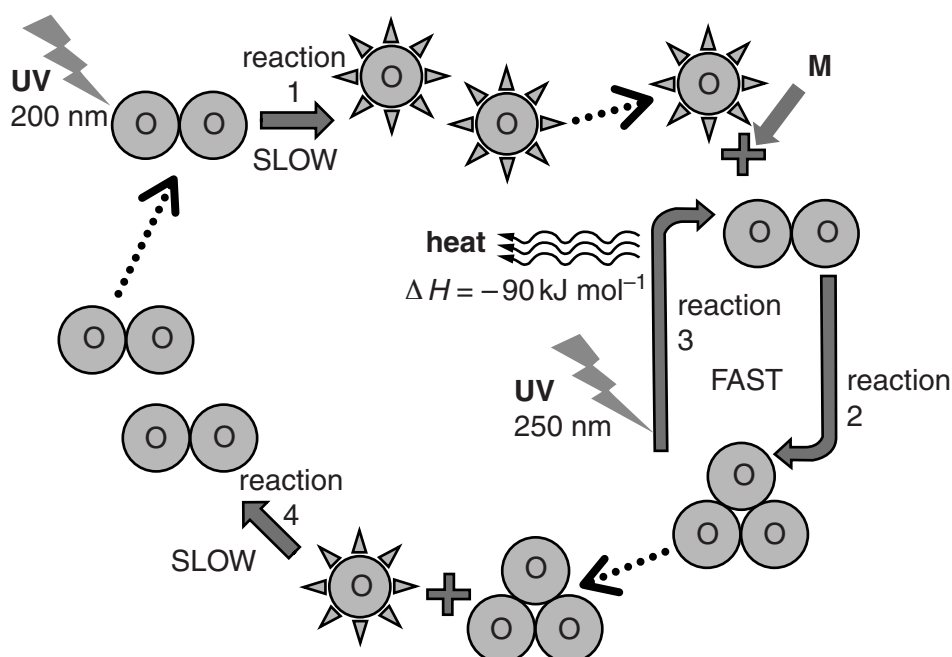


Fig. 3: Solid arrows indicate reactions, dotted arrows indicate that a molecule from one reaction goes on to take part in another reaction. M denotes the pressure required for reaction 2.

Image courtesy of Marlene Rau

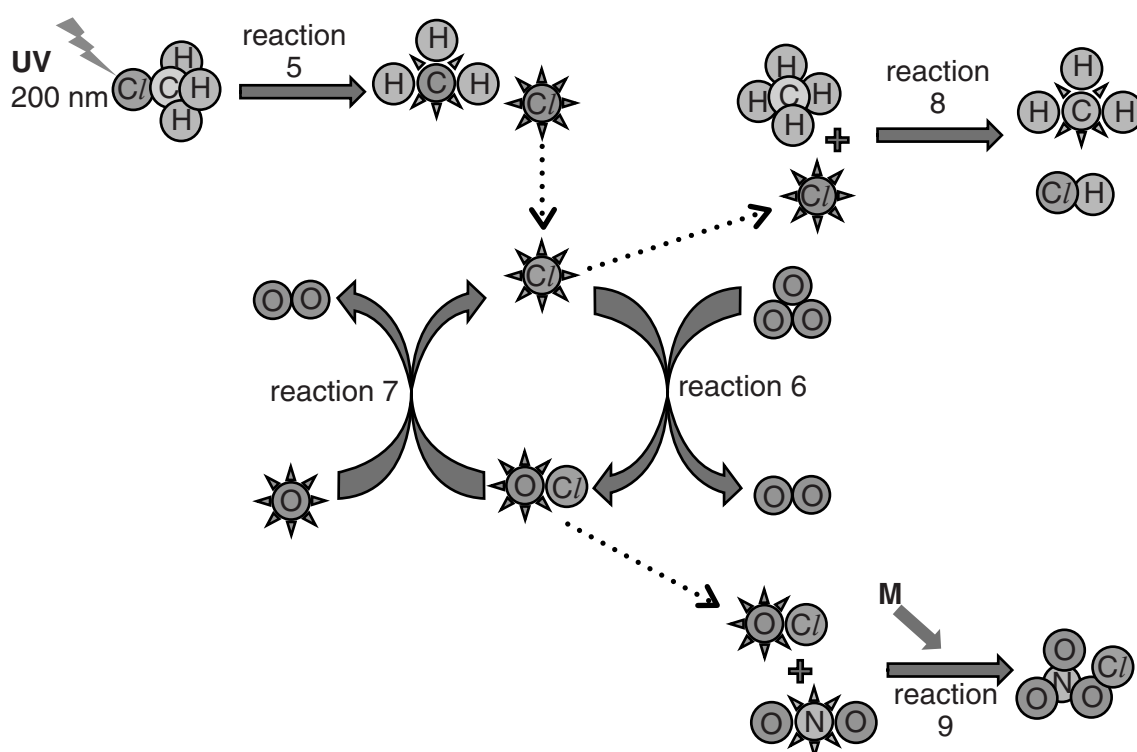
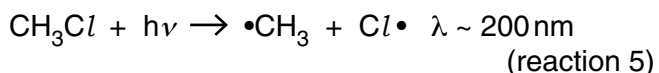


Fig. 4: Chlorine radicals (for example from reaction 5) enter a catalytic cycle (reactions 6 and 7) of net ozone decomposition, which can be terminated by reactions 8 and 9. Solid arrows indicate reactions, dotted arrows indicate that a molecule from one reaction goes on to take part in another reaction. M denotes the pressure required for reaction 9. Image courtesy of Marlene Rau

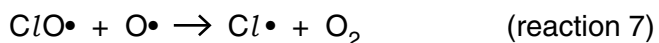
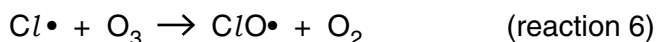
Natural catalytic cycles reduce the levels of ozone

In 1995, Paul Crutzen, Mario Molina and F Sherwood Rowland were awarded the Nobel Prize in Chemistry for their work on the formation and decomposition of ozone in the stratosphere. What had they learned? In the 1970s, Crutzen and others discovered the existence of natural catalytic cycles that speed up reaction 4 and reduce the amount of ozone in the stratosphere: water (H_2O), methane (CH_4), nitrous oxide (N_2O) and chloromethane (CH_3Cl) are released into the atmosphere from biological processes occurring on Earth's surface, and lead to the formation of radicals such as hydroxyl ($\text{HO}\bullet$), nitric oxide ($\text{NO}\bullet$) and chlorine ($\text{Cl}\bullet$), which catalyse the decomposition of ozone (see Fig. 4).

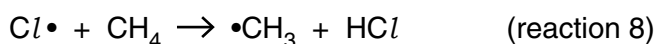
Reaction 5 shows how chloromethane releases chlorine radicals into the stratosphere through photolysis, and reactions 6 and 7 are an example of a catalytic cycle (see Fig. 4). The reactions of the other catalysts are analogous with reactions 6 and 7. Chloromethane is released in part by both marine and terrestrial organisms, such as red macroalgae, leafcutter ants, white rot fungi and higher plants and – after 30 to 40 years – can reach the upper stratosphere (around 40 km altitude) where it is broken down by sunlight (photolysis):



The resulting chlorine free radical ($\text{Cl}\bullet$) can then participate in a catalytic cycle:



Reactions 6 and 7 taken together are in fact equivalent to reaction 4, but happen much faster – in the case of the chlorine/chlorine monoxide ($\text{ClO}\bullet$) radical cycle, about 30,000 times faster. So why do these catalytic cycles not destroy all the ozone? The answer lies in the termination of these cycles via the formation of stable molecules:



Eventually, a chlorine free radical will encounter a methane molecule and react to form

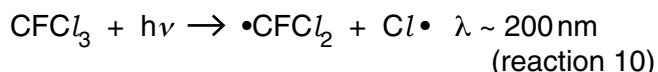
hydrochloric acid (HCl , reaction 8). Similarly, a chlorine monoxide radical will bind to a nitrogen dioxide radical, forming chlorine nitrate (ClONO_2 , reaction 9) – another pressure-dependent reaction that therefore works better at lower altitudes. Both hydrochloric acid and chlorine nitrate are very stable, and the removal of chlorine and chlorine monoxide radicals eventually stops the catalytic cycle.

The Antarctic ozone hole puzzle

It was not long before scientists realised that CFCs could trigger a similar catalytic cycle of ozone degradation: in 1974, Molina and Rowland not only warned that levels of CFCs continued to increase without regulation, but also predicted that CFCs would cause a significant additional loss of ozone at around 40 km altitude. However, when the ozone hole was finally found in 1985, it was in fact at around 20 km altitude, over the South Pole in the Southern Hemisphere springtime.

It soon emerged that chlorine free radicals from the CFCs were responsible, but many questions remained unanswered. Why did the hole occur over the Pole? If it occurred over the South Pole, why not also over the North Pole? Why only in spring? And why was the ozone hole at 20 km altitude instead of at 40 km, as predicted? After all, CFCs could not be broken down by sunlight at an altitude as low as 20 km, since the photon density was insufficient. For the same reason, not enough oxygen atoms are produced at this altitude for reaction 7 to occur. Many years of further research revealed the complete story.

First, chlorine free radicals released from the CFCs, eg



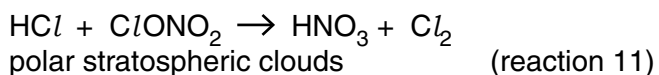
could react with methane (reaction 8) forming hydrochloric acid, or with ozone (reaction 6) forming chlorine monoxide radicals, and through reaction 9 could subsequently form chlorine nitrate. This sequence of reactions would increase the concentrations of hydrochloric acid and chlorine nitrate at around 40 km altitude globally.

Each Southern Hemisphere winter, the South Pole is plunged into darkness for approximately three months. The air in the stratosphere above the South Pole cools down; without UV radiation, reaction 3 does not occur, so no heat is released.

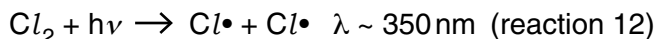
The air sinks and Earth's rotation causes it to spin and form a vortex as it does so, like water going down a plughole. This vortex is so strong that no air from outside can get in, and no air from inside can get out. Air that is rich in hydrochloric acid and chlorine nitrate from 40km altitude is drawn down into this cold and dark vortex.

In the extreme cold of the polar winter, the air in this vortex becomes so cold that below -78°C (195K) and at an altitude of 15–25km, polar stratospheric clouds form from water and/or acid ice crystals.

The first peculiar bit of chemistry is that hydrochloric acid and chlorine nitrate can adsorb onto polar stratospheric clouds and undergo a fast heterogeneous reaction, producing nitric acid (HNO_3) that becomes incorporated into the ice crystals, whilst the chlorine (Cl_2) is released back into the gas phase.



This reaction can take place all winter, if it is cold enough to form polar stratospheric clouds. When the sunshine returns in spring, there are plenty of chlorine molecules at around 15–25km altitude, which are photolysed to produce chlorine radicals:



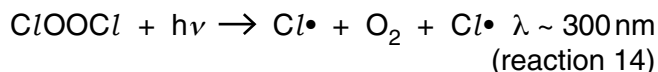
and subsequently chlorine monoxide radicals via reaction 6.

However, in the polar spring, reaction 7 (the formation of chlorine radicals and oxygen molecules from chlorine monoxide radicals and oxygen radicals) is very slow, since there are so few oxygen atoms present due to the lack of 200nm photons at this altitude, and here is where

a second peculiar piece of chemistry occurs. At low temperatures, such as in the polar vortex – which is still very cold even in spring – chlorine monoxide radicals can form a dimer, chlorine peroxide ($\text{ClOOC}\cdot\text{Cl}$):



This dimer is unstable at room temperature but forms quite readily at low temperatures (below -30°C) and can be photolysed:



So even though reaction 7 cannot occur, reaction 14 provides a way to regenerate chlorine free radicals with the help of light, and the catalytic cycle for ozone depletion can start in earnest now that the sunshine has returned.

In what way does this differ from the natural catalytic cycles we looked at before – why is there a total removal of ozone at some altitudes in this vortex? First, reaction 8 (which removes chlorine radicals and can terminate the cycle) is very slow at the low temperatures found in the vortex, and therefore ineffective. Second, all the nitrogen dioxide required for reaction 9 (which could likewise terminate the cycle, through the formation of ClONO_2) has been converted to nitric acid throughout the winter (eg through reactions 9 and 11) and it is not available to be regenerated since there is no upward flow in the vortex (at the base of the vortex, air flows from the South Pole to the Equator, where the upward flow takes place). Therefore the cycle carries on unchecked and destroys all the ozone at that level. Finally, without ozone, reaction 3, which would otherwise warm this region, is absent, and so the vortex lasts well into the spring, exacerbating the ozone depletion.

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