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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

F314530113

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.

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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).

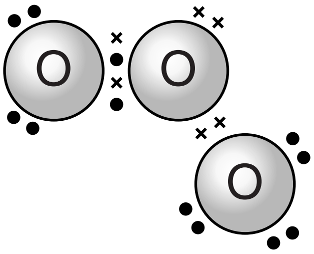

Fig. 1: 'Dot-and-cross' diagram for the bonding in ozone.

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 (hν) with a wavelength around 200 nm and dissociates into two oxygen atoms (O•) (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).

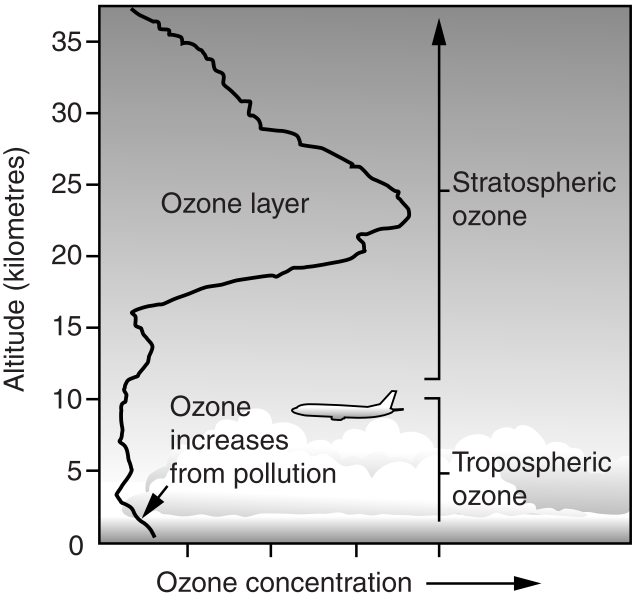

Fig. 2: Most ozone is in the stratosphere. Near Earth's surface, ozone levels increase due to pollution from human activities.

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.

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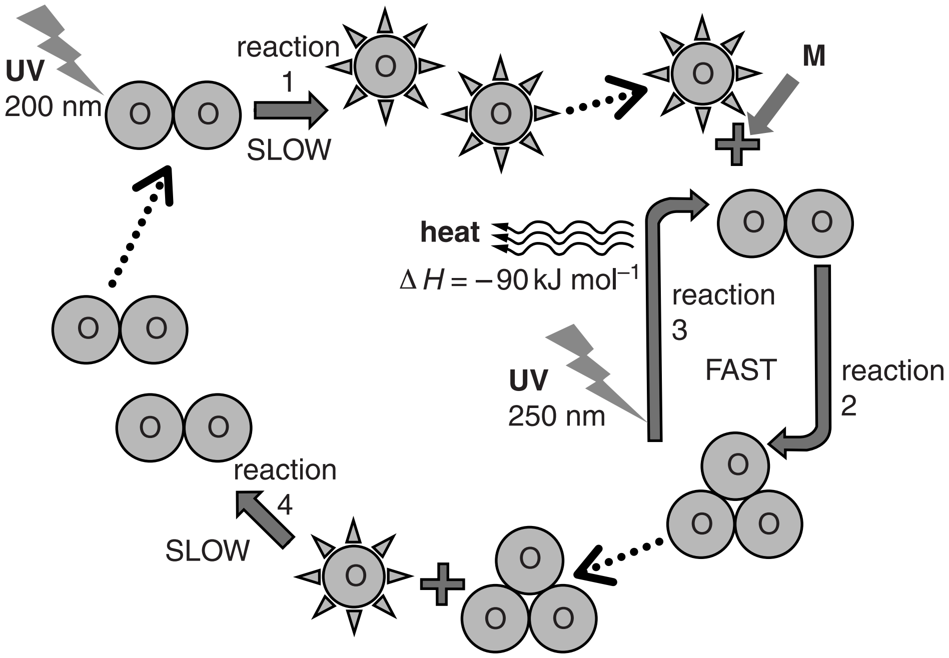
UV
200 nm
reaction
1
SLOW
M
heat
$\Delta H = -90\,\text{kJ mol}^{-1}$
reaction
3
FAST
UV
250 nm
reaction
2
reaction
4
SLOW
O

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

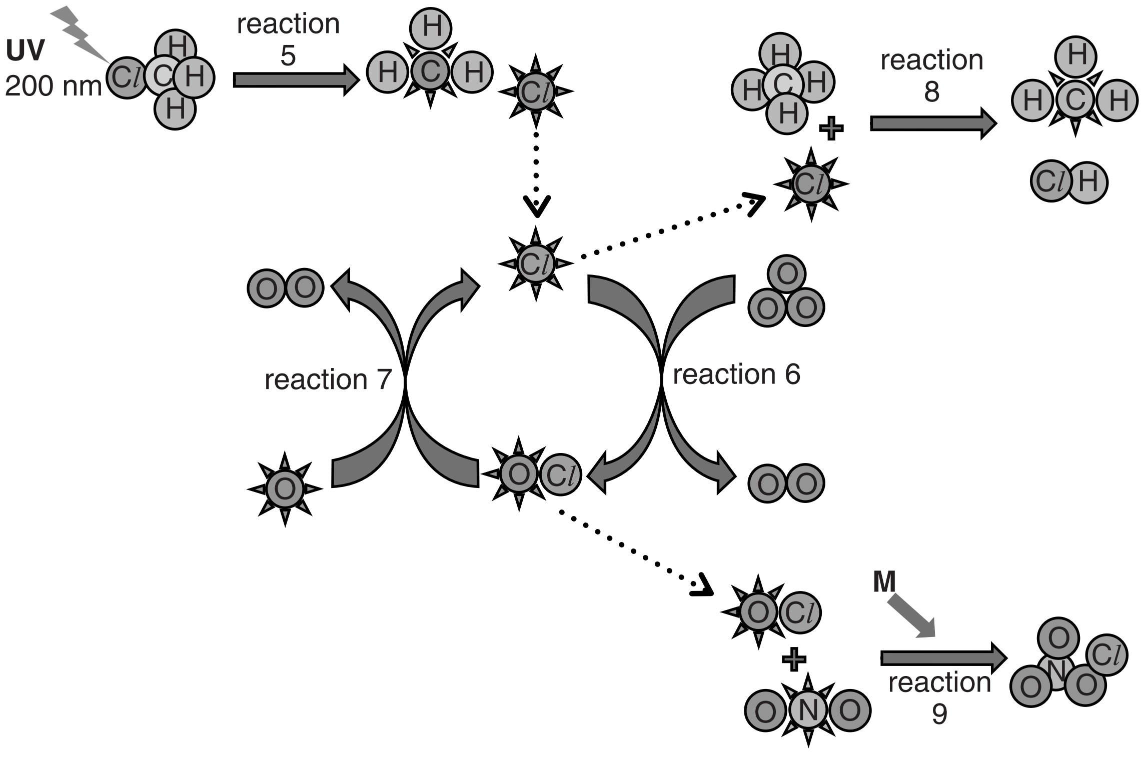
UV
200 nm
reaction
5
reaction
8
reaction 7
reaction 6
M
reaction
9
H
C
Cl
O
N

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 (HO•), nitric oxide (NO•) and chlorine (Cl•), 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):

$$CH_3Cl + h\nu \rightarrow \bullet CH_3 + Cl\bullet \quad \lambda \sim 200\,\text{nm} \qquad \text{(reaction 5)}$$

The resulting chlorine free radical (Cl•) can then participate in a catalytic cycle:

$$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2 \qquad \text{(reaction 6)}$$

$$ClO\bullet + O\bullet \rightarrow Cl\bullet + O_2 \qquad \text{(reaction 7)}$$

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 (ClO•) 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:

$$Cl\bullet + CH_4 \rightarrow \bullet CH_3 + HCl \qquad \text{(reaction 8)}$$

$$ClO\bullet + \bullet NO_2 \rightarrow ClONO_2 \qquad \text{(reaction 9)}$$

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

$$CFCl_3 + h\nu \rightarrow \bullet CFCl_2 + Cl\bullet \quad \lambda \sim 200\,\text{nm} \qquad \text{(reaction 10)}$$

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.

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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 40 km 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 (195 K) and at an altitude of 15–25 km, 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.

$HCl + ClONO_2 \rightarrow HNO_3 + Cl_2$
polar stratospheric clouds (reaction 11)

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 15–25 km altitude, which are photolysed to produce chlorine radicals:

$Cl_2 + h\nu \rightarrow Cl\bullet + Cl\bullet \quad \lambda \sim 350\,\text{nm}$ (reaction 12)

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 200 nm 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 ($ClOOCl$):

$ClO\bullet + ClO\bullet \rightarrow ClOOCl$ (reaction 13)

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

$ClOOCl + h\nu \rightarrow Cl\bullet + O_2 + Cl\bullet \quad \lambda \sim 300\,\text{nm}$
(reaction 14)

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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