



The Chemistry of the Ozone Layer

First, try deciding whether the following statements are true or false.

Statement	True	False
1. Ozone is produced by natural processes in the upper atmosphere.		
2. Ultra-violet radiation causes the bonds of ozone to break.		
3. Free radicals are formed when individual oxygen atoms react with chlorine molecules.		
4. Chlorofluorocarbons (CFCs) are stable, non-flammable, and low in toxicity.		
5. Ultra-violet radiation can cause the C-Cl bonds in CFCs to break.		
6. Chemists were against legislation to ban the use of CFCs.		
7. One chlorine atom can destroy thousands of ozone molecules.		
8. Chlorine atoms catalyse the decomposition of ozone.		

Statements 2, 3, and 6 are false and all the others are true.

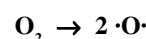
In order to succeed in this topic, you will need not only to understand the chemistry, but also to be able to discuss the issues surrounding the use of CFCs and the ozone layer in the upper atmosphere. Read each question carefully and make sure that your answer contains all the relevant points. Be sure to use the correct terms and, in particular, not to confuse molecules with atoms or radicals.

The main issues are:

- Chlorofluoroalkanes and chloroalkanes can be used as solvents. Chlorofluorocarbons (CFCs) were extensively used in aerosol cans, refrigerators and plastics in the past. CFCs were used because they are unreactive, have low flammability and have low toxicity. However, it was discovered that the use of these compounds was having a detrimental effect on the ozone layer.
- Although CFCs are stable in the troposphere (up to 10 km in altitude), they are liable to breakdown in the stratosphere (10 to 50 km altitude) where the ozone layer is situated. On breakdown they release chlorine atoms. These are **free radicals**, as they have unpaired electrons, and are highly reactive.
- High energy ultra-violet radiation present in the stratosphere causes the carbon-chlorine bonds in the CFCs to break and the chlorine radicals released react with ozone molecules, breaking them down. The chlorine radicals are regenerated in the process.
- The ozone layer plays a vital role for mankind as it absorbs high energy ultraviolet radiation. If this UV radiation reaches the surface of the Earth, it can initiate skin cancers in humans.

The Natural Processes Involving Ozone

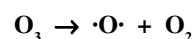
Ozone is constantly being formed and broken up again in the higher atmosphere by the action of ultraviolet light. Oxygen molecules are split up by ultraviolet light into individual oxygen atoms which are very reactive and are called **free bi-radicals** as they have 2 unpaired electrons.



These oxygen radicals then combine with oxygen molecules to make ozone.



Ozone can also be split up again into oxygen and a free radical under the action of ultraviolet light.



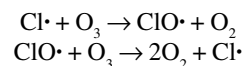
This formation and breaking up of ozone which goes on all of the time in the ozone layer, absorbs a lot of ultraviolet radiation thus preventing it from reaching the Earth's surface.

The Process Initiated by the Activities of Mankind

The catalytic reaction involving chlorine free radicals (atoms) from chloroalkanes, chlorofluoroalkanes and chlorofluorocarbons destroys the ozone, thus preventing it from absorbing the harmful ultraviolet radiation. This has contributed to the formation of a hole in the ozone layer and a higher incidence of skin cancer in humans living in areas beneath the hole.

Legislation to ban the use of CFCs was supported by chemists, who have now successfully developed alternative chlorine-free compounds.

The breaking of carbon-chlorine bonds in CFCs causes chlorine atoms to be formed as free radicals. This is an initiation step, (analogous to the initiation step in the reaction of methane with chlorine: $\text{Cl}_2 \rightarrow \text{Cl} \cdot + \cdot \text{Cl}$ under the action of ultraviolet light). Propagation equations such as the following may be used to show how the chlorine free radicals catalyse the decomposition of ozone, as the $\text{Cl} \cdot$ radicals react with the ozone to give oxygen but are themselves reformed at the end, thus acting like a catalyst.



The highly reactive chlorine radical causes an ozone molecule to be broken down to form oxygen plus another radical, which can then break down another ozone molecule to give oxygen plus a chlorine radical. Thus the chlorine radical acts as a catalyst. These repeating cyclic reactions can also be referred to as a **chain reaction**.

Sample Questions

- Including equations in your answer, explain how the balance of oxygen and ozone in the stratosphere was altered by CFCs. (6marks)
- Explain why legislation to ban the use of CFCs was introduced. (4marks)
- Give the reaction conditions and write an equation to show how the ozone may be broken down in the stratosphere (in the absence of CFCs or other artificial compounds) (2 marks)
- Draw a dot and cross diagrams to show an oxygen radical and a chlorine radical. (2 marks)
- Explain how the introduction of CFCs into the stratosphere caused the breakdown of ozone. (3 marks)
- Why do hydrofluorocarbons, which may be used instead of chlorofluorocarbons (CFCs), not cause significant breakdown of ozone in the stratosphere? (2 marks)
- Why is the ozone layer in the stratosphere of benefit to people? (2 marks)

Answers

- You should have included the following points in your answer. CFCs absorb ultraviolet radiation (1 mark)
This causes the CFC to break down to give chlorine free radicals/atoms, for example $\text{CCl}_2\text{F}_2 \rightarrow \cdot\text{CClF}_2 + \text{Cl}\cdot$ (1 mark)
Chlorine radicals/atoms react with the ozone in the ozone layer, and produce $\text{ClO}\cdot$ and oxygen
 $\text{Cl}\cdot + \text{O}_3 \rightarrow \text{ClO}\cdot + \text{O}_2$ (1 mark)
Chlorine radicals are generated by the reaction of $\text{ClO}\cdot$ with ozone. $\text{ClO}\cdot + \text{O}_3 \rightarrow \text{Cl}\cdot + 2\text{O}_2$ (1 mark)
In the absence of CFCs, ozone is broken down by photolysis producing oxygen atoms, but this reaction is balanced by the production of ozone when oxygen biradicals/atoms and oxygen react. $\text{O}_3 \rightleftharpoons \text{O}_2 + \cdot\text{O}\cdot$ (1 mark)
The presence of CFCs means that a higher proportion of ozone is broken down due to catalytic action/chain reaction. (1 mark)
Read the exam paper carefully, as one of the marks may be given for a clear answer in good English, showing a clear understanding of the important ideas involved such as (a) free radicals (b) chain reaction or (c) the Cl radical acting as a catalyst which is being regenerated.
- CFCs reach the stratosphere/upper atmosphere where they release chlorine atoms/radicals due to the high energy ultraviolet light from the Sun. (1 mark)
The chlorine atoms/radicals cause the breakdown of ozone and are also regenerated in the reaction/act as a catalyst. (1 mark)
The loss of ozone in the ozone layer/formation of a hole in the ozone layer prevents/lessens the absorption of high energy ultraviolet light by the ozone. (1 mark)
The ultraviolet light reaching the Earth can cause skin cancer. (1 mark)
- Under the action of ultraviolet light (1 mark)
 $\text{O}_3 \rightarrow \cdot\text{O}\cdot + \text{O}_2$ (1 mark)
- $\cdot\ddot{\text{O}}\cdot$ (1 mark) $\cdot\ddot{\text{Cl}}\cdot$ (1 mark)
- Chlorofluorocarbons are highly stable compounds which reach the stratosphere without breaking down. The high energy ultraviolet radiation in the stratosphere causes the C-Cl bonds in the CFCs to be broken. (1 mark)
Chlorine radicals/atoms break down the ozone
 $\text{Cl}\cdot + \text{O}_3 \rightarrow \text{ClO}\cdot + \text{O}_2$ (1 mark)
The chlorine radicals/atoms are regenerated/act as a catalyst in the process and so relatively few can destroy very many/millions of ozone molecules $\text{ClO}\cdot + \text{O}_3 \rightarrow 2\text{O}_2 + \text{Cl}\cdot$ (1 mark)
- They are not broken down in the troposphere/ lower atmosphere (1 mark)
because they contain stronger C-H and C-F bonds, not C-Cl bonds (1 mark)
- The ozone absorbs ultraviolet/UV radiation (1 mark)
UV radiation can cause skin cancers (1 mark)

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