Ozone hole problem

**Principles**

The ozone layer in the stratosphere (15 - 50 km high) is of vital significance for life on Earth. Without its protective effect, any life outside of water would not be possible due to the powerful short-wave UV radiation. The ozone layer acts as a filter for radiation of wavelength 220 to 310 nm. All of the UVC radiation (220 - 280 nm) and most of the UVB radiation (280 - 320 nm) is absorbed in this way.

A reduction in the ozone concentration (ozone depletion, ozone hole) therefore leads to an increase in the intensity of biologically effective UVB radiation. With plants, this can lead to damage and therefore to reduced crop yields. Phytoplankton (types of algae in the upper water layer of the ocean) is also affected - an important member in the marine food chain. As it also absorbs considerable quantities of carbon dioxide, it is an essential component of the carbon cycle and is associated with the greenhouse effect.

Increased UVB radiation can lead to eye and skin damage in humans and animals. The skin ages more quickly with frequent exposure. As the DNA molecules of skin cells react in a particularly sensitive way, this can result in cell changes going even as far as skin cancer. The immune system is also weakened through long-term exposure to UV radiation. It can therefore generally be said that, with an increase in UVB radiation and in the length of exposure, the risks to health increase.

Ozone forms in the stratosphere through the effect of strong UV radiation on oxygen.

\[
O_2 \xrightarrow{h^\nu} O + O \quad (\lambda < 240 \text{ nm})
\]

The very reactive oxygen atoms react in the presence of an additional neutral reaction partner M (e.g. nitrogen or oxygen) with \( O_2 \) molecules to form ozone.

\[
O + O_2 + M \rightarrow O_3 + M
\]

The resulting ozone can be split again by wavelengths below 310 nm.

\[
O_3 \rightarrow O + O_2 \quad (\lambda < 310 \text{ nm})
\]

A further possibility of depletion is the reaction of ozone molecules with oxygen atoms.

\[
O_3 + O \rightarrow 2 O_2
\]

These four reaction steps are referred to as the Chapman mechanism. They show that the concentration of ozone can be held in a stationary equilibrium by constant creation and depletion.

As the actual quantity of ozone is distinctly below that expected theoretically, there must be a further mechanism which leads to an additional depletion of ozone. As we now know, this is the catalytic depletion by various trace gases, with CFCs (chlorofluorocarbons) leading the way. These molecules form highly effective catalysts when split (this is a chlorine atom in

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**Aims of the experiment**

- To measure the absorption of UVC radiation by ozone
- To prove the destruction of ozone by CFCs
- To synthesize ozone from atmospheric oxygen

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**Chemical engineering**

Chemistry and the environment

*Global environmental problems*

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**Fig. 1** Set-up of the experiment
During the experiment, do not under any circumstances look into the UVC beam. Note: Do not look directly into the UVC beam at any time.

This example), which can promote a reaction a thousand times before they are "used up".

\[ \text{CF}_2\text{Cl} \rightarrow \text{CF}_3 + \text{Cl} \quad (\lambda < 220 \text{ nm}) \]

The depletion of ozone occurs in the following way:

\[ \text{O}_3 + \text{Cl} \rightarrow \text{O}_2 + \text{ClO} \]

\[ \text{ClO} + \text{O} \rightarrow \text{O}_2 + \text{Cl} \]

Further catalysts are hydroxide (OH), nitrogen monoxide (NO) and bromide (Br). On the whole, the reactions occurring in the ozone layer are very complex: 40 different substances react with each other in over 200 reactions, which are also very dependent on temperature as well as radiation.

An additional problem lies in the fact that the trace gases released rise only very slowly into the stratosphere. To reach it takes around 5 - 10 years. A similar length of time passes until measures to reduce harmful trace gases take effect, and during which CFC emissions continue to have an effect.

Owing to their chemically inert nature and their particular physical properties, CFCs have been used as coolants, foaming agents for plastics and propellants. The quantity of CFCs used has been greatly reduced and their distribution officially regulated to reduce further damage to the ozone layer.

In this experiment, the effect of ozone as a UV filter is shown and the depletion of ozone by CFCs is demonstrated. Ozone is created from pure oxygen or atmospheric oxygen through silent electric discharge using a high voltage. As real CFCs are for the most part banned, dichloromethane (CH₂Cl₂) is used as a substitute in this experiment. This produces similar results in the experiment, but is not harmful to the ozone layer as it is broken down photochemically already in the troposphere.

Risk assessment

During the experiment, do not enter any circumstances look into the UVC beam.

<table>
<thead>
<tr>
<th>Equipment and chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 UV-IR-VIS experiment kit ........................................ 666 265</td>
</tr>
<tr>
<td>1 Pocket-CASSY 2 Bluetooth ........................................ 524 018</td>
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<tr>
<td>1 CASSY Lab 2 ..................................................... 524 220</td>
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<tr>
<td>1 Battery for Pocket-CASSY 2 Bluetooth .......................... 524 019</td>
</tr>
<tr>
<td>1 Bluetooth dongle .................................................. 524 0031</td>
</tr>
<tr>
<td>1 Lux adapter S ....................................................... 524 0511</td>
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<tr>
<td>1 UVC sensor .......................................................... 666 246</td>
</tr>
<tr>
<td>1 Spark gap supply unit ............................................... 667 818</td>
</tr>
<tr>
<td>1 Safety connection lead 50 cm, red ............................... 500 621</td>
</tr>
<tr>
<td>1 Safety connection lead 50 cm, blue ............................... 500 622</td>
</tr>
<tr>
<td>1 Crocodile clips, insulated, set of 2 .............................. 667 489</td>
</tr>
<tr>
<td>1 Rubber bellows, single bulb ........................................ 667 241</td>
</tr>
<tr>
<td>1 Dosing syringe 1 ml .................................................. 665 957</td>
</tr>
<tr>
<td>1 Cannula 0.6 mm Ø, set of 10 ........................................ 603 030</td>
</tr>
<tr>
<td>1 Dichloromethane, 250 ml ............................................. 671 6600</td>
</tr>
<tr>
<td>Also required: PC with Windows XP/Vista/7/8</td>
</tr>
</tbody>
</table>

Set-up and preparation of the experiment

Set-up of the apparatus

1. The apparatus is set up as can be seen in Fig. 1.
2. Position the round cuvette of the UV-IR-VIS experiment kit with two supports immediately in front of the exit port of the UVC beam.
3. Place the UVC sensor with holder in front of the cuvette window.
4. Connect the spark gap supply unit using safety cables and crocodile clips to the metal contacts of the round cuvette.
5. Connect the UV-IR-VIS experiment kit via the plug-in power supply and switch the UVC lamp on via the step switch.

Preparation of the experiment

1. Some settings must be made in CASSY Lab before the experiment.
2. Firstly, under the sensor input settings, select the parameter Light Intensity E (UVC) with the measurement range 0 – 10 W/m².
3. On the tab Parameters/Formula/FTT, enter the new variable Light Intensity. Enter the following values for this:
   Mean value of E over 20 s
   Symbol: E
   Units: W/m² from 0 – 1.2 W/m²
   Decimal places: 2
   4. On the Display tab, label the y-axis with the variable E’.
   5. In the Measurement Parameters dialogue window, select Automatic recording of the measured values, and 1 second for the measurement interval.

Performing the experiment

Absorption of UVC radiation by ozone

1. Before starting the measurement, remove the remaining air from the cuvette using the rubber bellows. Then close the cuvette with the two rubber bulbs.
2. When the value measured in CASSY Lab is constant for 3 minutes, the measurements can be started.

Dichloromethane

<table>
<thead>
<tr>
<th>Hazard statements</th>
</tr>
</thead>
<tbody>
<tr>
<td>H315 Causes skin irritation.</td>
</tr>
<tr>
<td>H319 Causes serious eye irritation.</td>
</tr>
<tr>
<td>H335 Causes respiratory irritation.</td>
</tr>
<tr>
<td>H336 May cause drowsiness or dizziness.</td>
</tr>
<tr>
<td>H351 Suspected of causing cancer.</td>
</tr>
<tr>
<td>H373 May cause damage to organs.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Precautionary statements</th>
</tr>
</thead>
<tbody>
<tr>
<td>P261 Avoid breathing dust/fume/gas/mist/vapour/spray.</td>
</tr>
<tr>
<td>P281 Use personal protective equipment as required.</td>
</tr>
<tr>
<td>P305+351+338 If in eyes: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.</td>
</tr>
</tbody>
</table>
3. Start recording the measured values in CASSY Lab.
4. Then switch the spark gap supply unit to continuous sparking (red LED illuminates).
   **Note:** It is absolutely essential that a silent electric discharge is used for the experiment. This means that both needles must be so far apart that no visible sparks can be detected.
5. Mark the time of switch-on by placing a vertical line in the graph. To do this, right click using the mouse and select the item Evaluation. Then select a vertical line here and mark it in the graph.
6. The spark gap can be switched off after 5 - 10 minutes. Place a new mark in the graph.
7. The recording of the measured values can be stopped after a further 5 - 10 minutes.

### Ozone depletion by CFCs (here, dichloromethane)
1. The measurement set-up for the measurement of ozone depletion by CFCs remains the same as before for the absorption of UVC radiation by ozone.
2. Before starting the measurement, remove the remaining air from the cuvette using the rubber bellows. Then close the cuvette with two rubber bulbs.
3. When the value measured in CASSY Lab is constant for 3 minutes, the measurements can be started.
4. Start recording the measured values in CASSY Lab.
5. Then switch the spark gap supply unit to continuous sparking (red LED illuminates).
   **Note:** It is absolutely essential that a silent electric discharge is used for the experiment. See Part 1 of the experiment.
6. Mark the time of switch-on by placing a vertical line in the graph. To do this, right click using the mouse and select the item Evaluation. Then select a vertical line here and mark it in the graph.
7. Briefly shake the closed dichloromethane bottle. If the measured value remains constant, open the bottle and with the dosing syringe remove 1 ml of vapour from the gas phase (headscape) above the liquid.
8. Inject the contents of the syringe into the round cuvette through the rear rubber bulb and insert another mark in the graph.
9. Stop the measurement after 3 - 5 minutes and switch the spark gap supply unit off.

### Observation

#### Absorption of UVC radiation by ozone

After switching the spark gap on, the discharge in the cuvette can be observed. After switch-on, a distinct increase in the absorption of UVC radiation can also be observed (Fig. 2, Mark 1). This decreases again, however, after the spark gap is switched off (Mark 2).

#### Ozone depletion by CFCs (here, dichloromethane)

After switching the high voltage on, it can be observed as in the previous experiment that ozone is formed which results in an increase in absorption of the UVC radiation (Fig. 2, Mark 1). However, this changes after injecting dichloromethane, although the high voltage is still switched on (Mark 2).

### Evaluation

#### Absorption of UVC radiation by ozone

Switching the spark gap on and off was marked in the graph by vertical lines. By reference to both marks and the shape of the curve, a statement can be made on the protective effect of the ozone against UVC radiation. With increasing ozone, more UVC radiation is absorbed.

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**Results**

#### Absorption of UVC radiation by ozone

The result of the absorption of UVC radiation by ozone can be seen in Fig. 2.

![Graph showing the absorption of UVC radiation by ozone](image)

After the spark gap is switched on, atmospheric oxygen contained in the cuvette forms ozone through the silent electric discharge.

\[ O_2 \rightarrow O + O \]
\[ O + O_2 + M \rightarrow O_3 + M \]

Here, the high voltage takes over the role of the strong radiation in the stratosphere, which otherwise leads to the formation of ozone.

The ozone formation reaction outweighs the depletion reaction in this case.

\[ O_3 \rightarrow O + O_2 \]

Through the increasing ozone concentration in the cuvette, the incident UVC radiation will be increasingly absorbed. This leads to a reduction in value of the variable E, which can be observed in the graph (Section 1). After the spark gap is switched off again, no further ozone can be formed. From this point in time, the depletion reaction of ozone is predominant. With the decrease in ozone concentration in the cuvette, a decrease in absorption of UVC radiation also occurs. This decrease leads to a rise in value of the variable E in the graph (Section 2).

This experiment was able to demonstrate the protective effect of the ozone layer.

#### Ozone depletion by CFCs (here, dichloromethane)

The results of the measurements for ozone depletion by CFCs can be seen in Fig. 3.
As already shown in the first experiment, ozone is formed from the atmospheric oxygen contained in the cuvette through the silent electric discharge after switching on the spark gap. As a consequence, this causes an increase in absorption of UVC radiation (Section 1). In this part of the experiment, gaseous dichloromethane is injected after 5 - 10 minutes. This takes over the role of CFCs in the atmosphere, by way of example. The chlorine atoms contained in the dichloromethane form highly effective catalysts through splitting of the dichloromethane molecule.

These chlorine atoms eventually cause depletion of the previously formed ozone. The depletion of ozone takes place in the following way:

$$O_3 + Cl \rightarrow O_2 + ClO$$
$$ClO + O \rightarrow O_2 + Cl$$

Despite the continuous supply of energy from the spark gap, the intensity of the UVC radiation increases at the sensor. This means that the depletion of ozone is clearly predominant over the formation of new ozone (Section 2).

In this experiment, the depletion of ozone and the increase in intensity of UVC radiation associated with this can be clearly proven using dichloromethane as a CFC replacement. This experiment clarifies by way of example the problem of ozone depletion in the atmosphere.

**Cleaning and disposal**

There are no special instructions to follow.