Creation of Ozone in Stratosphere

Above stratosphere most of the oxygen absorbs UV-C and exists as O atoms

\[ \text{O}_2 + \text{hv} \rightarrow 2\text{O} \quad \text{495 kJ/mole (241 nm)} \]

Because of the high concentration of \text{O}_2 in stratosphere, any O atom present gets converted to \text{O}_3

\[ \text{O}_2 + \text{O} \rightarrow \text{O}_3 \]
\[ \text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 \]

A third molecule M (N\textsubscript{2} or H\textsubscript{2}O) facilitates as a heat energy carrier.

Because of the temperature inversion **vertical mixing** of air is a slow process in stratosphere than in troposphere.
Destruction of Ozone in Stratosphere

Ozone absorbs UV light below 320 nm and undergoes dissociation

\[ \text{O}_3 + \text{hv} \rightarrow \text{O}_2^* + \text{O}^* \]

Both \( \text{O}_2 \) and \( \text{O} \) produced via UV photon are in the excited state

Determine the longest wavelength that is needed for the dissociation of \( \text{O}_3 \)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_3 \rightarrow \text{O}_2 + \text{O} )</td>
<td>105</td>
</tr>
<tr>
<td>( \text{O} \rightarrow \text{O}^* )</td>
<td>190</td>
</tr>
<tr>
<td>( \text{O}_2 \rightarrow \text{O}_2^* )</td>
<td>95</td>
</tr>
</tbody>
</table>

\[ \text{O}_3 \rightarrow \text{O}_2^* + \text{O}^* \quad 390 \text{ kJ/mol} \]

\[ \lambda = \frac{119627 \text{ kJ nm mol}^{-1}}{390 \text{ kJ mol}^{-1}} = 307 \text{ nm} \]

The Steady State Analysis

Rate of change of an intermediate = Rate of formation - rate of destruction

\[ \text{A} \rightarrow \text{B} \quad (1) \]
\[ \text{B} \rightarrow \text{C} \quad (2) \]

Rate of change of B = \( k_1[\text{A}] - k_2[\text{C}] \)

At Steady State the rate of change (d[B]/dt) is zero

\[ \therefore \text{Rate of formation} - \text{Rate of destruction} = 0 \]

Or Rate of formation = Rate of destruction

In the above example,

\[ k_1[\text{A}] = k_2[\text{C}] \text{ or } [\text{A}]/[\text{C}] = k_2/k_1 \]
**What is the difference between an equilibrium and steady state?**

**Equilibrium System (A=B)**

Reactants  \[ \xrightarrow{A} \]  Products

Reactant & Product Concentrations remain constant

An equilibrium system is a closed system in which the forward and backward reactions occur at the same time and at equal rates.

**Steady State (A=B)**

Reactants  \[ \xrightarrow{A} \]  Intermediate  \[ \xrightarrow{B} \]  Products

Concentration of Intermediates remain constant
Most of the atmospheric reactions driven by sunlight are steady state reactions

A steady state is an open system in which an intermediate is formed and destroyed at the same rate in separate reactions.

**Steady State Analysis for Ozone in the Atmosphere: Chapman Mechanism**

\[ \begin{align*}
O_2 & \rightarrow 2O \quad (1) \\
O + O_2 + M & \rightarrow O_3 + M \quad (2) \\
O_3 & \rightarrow O_2 + O \quad (3) \\
O_3 + O & \rightarrow 2O_2 \quad (4)
\end{align*} \]

Since O is consumed or formed in all the reactions we can assume that it is in the steady state

**Rate of change of O = 2(rate1) –rate2 + rate3 – rate 4 = 0 \quad (A)**

Similarly,

**Rate of change of O_3 = rate2 – rate3 –rate4 = 0 \quad (B)**

\[ (A) + (B): \quad 2(rate1) – 2(rate4) =0 \]

By expressing rate in terms of rate constant and concentration

\[ 2k_1[O_2] – 2k_4[O_3][O] =0 \]

OR \[ [O_3][O] = k_1[O_2]/k_4 \quad (C) \]
From previous analysis,

\[ 2(\text{rate}1) - \text{rate}2 + \text{rate}3 - \text{rate}4 = 0 \quad (A) \]

Rate of change of \( \text{O}_3 \) = \( \text{rate}2 - \text{rate}3 - \text{rate}4 = 0 \quad (B) \]

\[ [\text{O}_3][\text{O}] = k_1[\text{O}_2]/k_4 \quad (C) \]

\[(A) - (B): \quad 2\text{rate}1 - 2\text{rate}2 + 2\text{rate}3 = 0 \]

or \[ \text{rate}3 = \text{rate}2 - \text{rate}1 \]

since \( \text{rate}1 \ll \text{rate} 2 \) and \( \text{rate} 3 \), we can neglect the term

\[ \text{rate}3 = \text{rate}2 \]

\[ k_3[\text{O}_3] = k_2[\text{O}][\text{O}_2][\text{M}] \]

or \[ [\text{O}_3]/[\text{O}] = k_2[\text{O}_2][\text{M}]/k_3 \quad (D) \]

\[(C)x(D): \quad [\text{O}_3]^2 = [\text{O}_2]^2[M]k_1k_2/k_3k_4 \]

or \[ [\text{O}_3]/[\text{O}_2] = [M]^{0.5}(k_1k_2/k_3k_4)^{0.5} \quad (E) \]

At Steady State, \[ [\text{O}_3]_{ss}/[\text{O}_2]_{ss} = [M]^{0.5}(k_1k_2/k_3k_4)^{0.5} \quad (E) \]

The steady state ratio of \( \text{O}_3 \) to \( \text{O}_2 \) depend on
- square root of air density
- proportional to square root of product of \( k_1 \) & \( k_2 \) corresponding to \( \text{O} \) and \( \text{O}_3 \) production
- inversely proportional to square root of product of \( k_3 \) &\( k_4 \)
- based on experimental values of \( k \) and \( M \), maximum \( [\text{O}_3] \) is of the order of \( 10^{-4} \) M

\[ M \text{ decreases with increasing altitude} \]

\[ \text{Absorption of UV-C (and } k_1 \text{) decreases with decreasing altitude} \]

Peak concentration of ozone is expected at altitude of \( \sim 40 \) km
(Actual peak is observed at 25 km because of the movement of \( \text{O}_3 \) downwards)
**Concentration of Atomic Oxygen**

**From (E) and (C)**

\[ [O]_{ss} = \left( \frac{k_1 k_3}{k_2 k_4} \right)^{0.5} / [M]^{0.5} \]

- \([O]_{ss}\) increases with increasing altitude as \([M]\) declines
- \(k_1\) and \(k_3\) increase with altitude

\[ \therefore \ O \text{ atoms dominate over } O_3 \text{ at higher altitudes (> 50 km).} \]

**Comparison of stratosphere ozone concentration as a function of altitude**

- The actual destruction of ozone is more than the prediction
The Chapman theory, however, overestimates the ozone contents. Thus, there must be other chemical reactions contributing to the reduction of the ozone content.

In 1970, Paul Crutzen showed that the nitrogen oxides NO and NO\textsubscript{2} react catalytically (without themselves being consumed) with ozone, thus accelerating the rate of reduction of the ozone content.

\[
\begin{align*}
\text{NO} + \text{O}_3 &\rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{O} &\rightarrow \text{NO} + \text{O}_2 \\
\text{O}_3 + \text{uv-light} &\rightarrow \text{O}_2 + \text{O} \\
\hline
\text{Net result:} &\rightarrow 2\text{O}_3 \rightarrow 3\text{O}_2
\end{align*}
\]

*Note NO acts as a catalyst and requires O atom for regeneration—referred as Mechanism I*

Two important chemistry contributions leading to the discovery of the link between Freon and ozone depletion

- James Lovelock (England) had developed a highly sensitive device of measuring extremely low organic gas contents in the atmosphere, the electron capture detector. Using this he could now demonstrate that the exclusively man-made, chemically inert, CFC gases had already spread globally throughout the atmosphere.

- Richard Stolarski and Ralph Cicerone (USA) had shown that free chlorine atoms in the atmosphere can decompose ozone catalytically in similar ways as nitrogen oxides do.
Spray cans and refrigerators damage the ozone layer

- In 1974, Molina and Rowland proposed in their *Nature* article that the chemically inert CFC could gradually be transported up to the ozone layer, there to be met by such intensive ultra-violet light that they would be separated into their constituents, notably chlorine atoms.
- They calculated that if human use of CFC gases was to continue at an unaltered rate the ozone layer would be depleted by many percent after some decades.

Joe Farman and his colleagues revealed a dramatic and unpredicted decline in stratospheric ozone in perhaps the most unexpected region of the globe - over the Antarctic in spring, and Farman suggested that it was due to gases emitted into the atmosphere by Man.


Using measurements of the total amount of ozone in a column of atmosphere above the BAS Halley Bay base at 76°S, dating back to the International Geophysical Year in 1957, Joe Farman showed that a dramatic decline in springtime ozone over the entire Antarctic continent had taken place, starting in the late 1970s, reaching ~30% by 1985.
Chlorofluorocarbons or CFCs (also known as Freon) are non-toxic, non-flammable and non-carcinogenic. They contain fluorine atoms, carbon atoms and chlorine atoms. The 5 main CFCs include:

- CFC-11 (trichlorofluoromethane - CFCl₃),
- CFC-12 (dichloro-difluoromethane - CF₂Cl₂),
- CFC-113 (trichloro-trifluoroethane - C₂F₃Cl₃),
- CFC-114 (dichloro-tetrfluoroethane - C₂F₄Cl₂), and
- CFC-115 (chloropentafluoroethane - C₂F₅Cl).

Chlorofluorocarbons have a lifetime in the atmosphere of about 20 to 100 years, and consequently one free chlorine atom from a CFC molecule can do a lot of damage, destroying ozone molecules for a long time. Although emissions of CFCs around the developed world have largely ceased due to international control agreements, the damage to the stratospheric ozone layer will continue well into the 21st century.
Ozone-depleting substances (CFCs, HCFCs, HBFCs, and halons) are numbered according to a system devised several decades ago and now used worldwide.

It provides very complex information about molecular structure and also easily distinguishes among various classes of chemicals.

For example, it is not intuitive that 1,1-dichloro-1-fluoroethane (CFCl₂-CH₃) is an ozone-depleting substance. The designation HCFC-141b, in contrast, immediately conveys its ozone-depleting nature while concisely describing its structure.

The prefix describes what kinds of atoms are in a particular molecule, the next step is to calculate the number of each type of atom. The key to the code is to add 90 to the number; the result shows the number of C, H, and F atoms. For HCFC-141b:

\[
141 + 90 = 2 \ 3 \ 1 \\
#C \ #H \ #F
\]

One more piece of information is needed to decipher the number of Cl atoms. All of these chemicals are saturated; that is, they contain only single bonds. The number of bonds available in a carbon-based molecule is \(2n(C) + 2\). Thus, for HCFC-141b, which has \(n=2\) carbon atoms, there are 6 bonds. Cl atoms occupy bonds remaining after the F and H atoms.

\[
\therefore \text{HCFC-141b has 2C, 3H, 1F, and 2Cl: } \text{HCFC-141b} = \text{C}_2\text{H}_3\text{FCl}_2
\]

Notice that the HCFC designation (hydro chloro fluoro carbon) is a good double-check on the decoding; this molecule does, indeed, contain H, Cl, F, and C. The "b" at the end describes how these atoms are arranged; different "isomers" contain the same atoms, but they are arranged differently. The letter designation for isomers.
Deduce the formula for the compounds with following code numbers 12, 113, 123, 134

a. 12 90+12= 102  C=1, H=0, and F= 2, \( \therefore \text{Cl}=2 \) \( \rightarrow \) CF₂Cl₂

b. 113 90+113= 203  C=2, H=0, and F= 3, \( \therefore \text{Cl}=3 \) \( \rightarrow \) C₂F₃Cl₃

c. 123 90+123= 213  C=2, H=1, and F= 3, \( \therefore \text{Cl}=2 \) \( \rightarrow \) C₂HF₃Cl₂

d. 134 90+134= 224  C=2, H=2, and F= 4, \( \therefore \text{Cl}=0 \) \( \rightarrow \) C₂H₂F₄

Other Ozone Depleting Substances

\( \text{CCl}_4 \) (Carbon tetrachloride)

Used as dry cleaning solvent

\( \text{CH}_3\text{-CCl}_3 \) (methyl chloroform)

Cleaning agent for metals

Halons

Bromine containing hydrogen free substances such as CF₃Br and CF₂BrCl used

Methyl bromide is used as a pesticide, fumigate crops (40% of world use is in the US)

They rise to stratosphere and decompose to produce Br\(^+\) – an efficient catalyst \( X' \) for \( O_3 \) depletion

Developing countries have agreed to reduce consumption, but not complete elimination

Meantime China & Korea have increased their production!
In 1985, nations agreed in Vienna to take “appropriate measures...to protect human health and the environment against adverse effects resulting or likely to result from human activities which modify or are likely to modify the Ozone Layer”, thus the Convention for the Protection of the Ozone Layer was born.

The main thrust of the Convention was to encourage research and overall cooperation among countries and exchange of information. Even so it took four years to prepare and agree. Twenty nations signed it in Vienna, but most did not rush to ratify it. The Convention provided for future protocols and specified procedures for Amendment and dispute settlement.

The Vienna Convention set an important precedent. For the first time nations agreed in principle to tackle a global environmental problem before its effects were felt, or even scientifically proven.

As the experts began to explore for specific measures to be taken, the journal 'Nature' published a paper in May 1985 by British scientists - led by Dr. Joe Farman - about severe ozone depletion in the Antarctic. The paper's findings were confirmed by American satellite observations and offered the first proof of severe ozone depletion and making the need for definite measures more urgent.

As a result, In September 1987, agreement was reached on specific measures to be taken and the Montreal
1987: Ozone agreement reached in Montreal


• In 1985, 49 countries met in Vienna to first discuss the protection of the ozone layer

• With the signing of the Montreal Protocol, two years later, 24 of these countries agreed to reduce the production and consumption of Chlorofluorocarbons (CFCs) by 50 per cent by 1999.

• The Protocol came into force on January 1st, 1989, when 29 countries and the European Economic Community (EEC), representing approximately 82 per cent of world consumption, had ratified it.

http://nnvl.noaa.gov/Media/Ozone/MontrealProtocolGraph_compressed.mov
off the mark.com by Mark Parisi

JEEPERS! IT'S GETTING PRETTY THIN...
MAYBE IF I COMB SOME OZONE FROM
HERE...