Chemistry 500: Chemistry in Modern Living

Topic 2: Protecting the Ozone Layer

Atoms and Light

Chemistry in Context, 2\textsuperscript{nd} Edition: Chapter 2, Pages 35-72

Chemistry in Context, 3\textsuperscript{rd} Edition: Chapter 2, Pages 45-92

Outline Notes by Dr. Allen D. Hunter, YSU Department of Chemistry, ©2000.
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2A What is Ozone?

- Ozone Formation

- Produced from a variety of processes:

  - Photochemical Smog (Topic 1)

  - High Voltage Electrical Discharges


\[
\text{Molecular Oxygen + Energy} \rightarrow \text{Ozone} \\
3 \text{O}_2 + \text{Energy} \rightarrow 2 \text{O}_3
\]

- Can be smelled at 10 ppb

- Arc Welding

- Lightning Storms

- Laser Printers

- Tesla Coils
➢ Allotropes

➢ Different forms of the same element

➢ They have different chemical structures

➢ Hence different chemical properties

➢ Examples include:

➢ Graphite (found in pencil lead) and Diamond (on rings) are different chemical forms of the element Carbon

➢ Molecular Oxygen and Ozone are different chemical forms of the element Oxygen
The Allotropes of the Element Oxygen

Molecular Oxygen, O₂

- A Diatomic Molecule
- Liquefies at -183 °C
- A light blue liquid
- Odorless

Ozone, O₃

- A Triatomic Molecule
- Liquefies at -112 °C
- A dark blue liquid
- Used in water purification and pulp and paper bleaching
- Characteristic Odor
2B What is the Structure of a Atom?

- Graphics from Text: Table 2.1, the Properties of Sub-Atomic Particles

- Overview of Atoms and Nuclei
  - Diagram Not to Scale!
  - Nucleus actually tremendously smaller than the electron cloud
  - The Electron Cloud includes both Core Electrons and Valence Electrons
Electrons, \( e^- \)
- Surround the Nucleus
- Mass of \( 1/1838 \) AMU
- Charge of -1

Protons, \( P^+ \)
- In the Nucleus
- Mass of 1 AMU
- Charge of +1

Neutron, \( n \)
- In the Nucleus
- Mass of 1 AMU
- Charge of 0

Neutron/Proton Ratio in Stable Nuclei
- Due to balance of Strong Nuclear Force and Electrostatic Force

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Evidence for this structure

- High Energy Diffraction / Collision Experiments

Rubber Baggie model of nucleus

Isotopes

- The same element (i.e., the same number of protons in the nucleus)
- Different Mass due to different number of Neutrons in the Nucleus
- Chemically Isotopes react extremely similarly

Examples:

- $^1$H (Hydrogen), $^2$H (D, Deuterium), and $^3$H (T, Tritium)
- $^{12}$C (common, 99%), $^{13}$C (rare, 1%, NMR), and $^{14}$C (very rare, produced in upper atmosphere, radioactive)
- $^{238}$U (non-radioactive) and $^{235}$U (radioactive)
The Periodic Table

- Use the Periodic Table to Evaluate the Number of $e^-$, $P^+$, and $n$ in each isotope

- Atomic Number $\Rightarrow$ The number of Electrons and Protons in the neutral atom

- Mass Number $\Rightarrow$ The total number of Protons and Neutrons

$^4\text{He} \Rightarrow$

$^4\text{He} \Rightarrow$

$^4\text{He} \Rightarrow$

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$^4\text{He} \Rightarrow$
Ask Students: For each of the following isotopes, give the total number of protons, neutrons, and electrons and then the number of valence electrons and core electrons.

Group Activity

$^7\text{Be} \implies \begin{align*} \# \text{e}^- &= \ \\
\# \text{P}^+ &= \ \\
\# n &= \end{align*}$

$^{13}\text{C} \implies \begin{align*} \# \text{e}^- &= \ \\
\# \text{P}^+ &= \ \\
\# n &= \end{align*}$

$^{19}\text{F} \implies \begin{align*} \# \text{e}^- &= \ \\
\# \text{P}^+ &= \ \\
\# n &= \end{align*}$

$^{29}\text{Si} \implies \begin{align*} \# \text{e}^- &= \ \\
\# \text{P}^+ &= \ \\
\# n &= \end{align*}$

$^{183}\text{W} \implies \begin{align*} \# \text{e}^- &= \ \\
\# \text{P}^+ &= \ \\
\# n &= \end{align*}$
2C How Do We Know Molecular Structures?

- How do we know molecular structures?

- Analytical Data

- Spectroscopic Methods
  - Sporting Methods
  - Specific absorption of light
  - NMR = Nuclear Magnetic Resonance (cf. MRI, Magnetic Resonance Imaging)
  - Infra-Red (IR)
  - Ultra Violet-Visible (UV-Vis)

- From the mid 1850s have know many molecular shapes but were not able to explain them other than to say the atoms were connected
- X-Ray Crystallography/Diffraction
  - Non-Sporting Method
  - Single Crystals
  - Hardware
  - Data Collection
  - Data Analysis
2D How Do We Explain Molecular Structures?

- Theories change over time to better fit the experimental data

- A Theory should explain all current data and predict future results

- Lewis Dot Structures
  - Lewis developed this theory to explain known molecular structures, reactivity data, and emerging ideas like electricity and radioactivity
  - Bonds were due to shared pairs of electrons
  - Lone Pairs of Valence Electrons remain on many atoms
  - Only the Valence Electrons Contribute to bonding
    - This accounts for the fact that elements underneath one another on the periodic table react similarly
Rigorous Method of Determining Lewis Dot Structures

- Count the total number of valence electrons for the molecules
- Distribute them around the atoms such that each atom gets as close to a complete Octet as possible
- An Octet is 8 for most elements but 2 for Hydrogen and Helium
- Some elements will allow / settle for greater or lesser than 8 electrons but we won’t see these in Chem. 500
Quick and Dirty Method for getting Lewis Structures

An oversimplification that can break down but works well for most Organic Compounds

Bond Lengths

Bond Angles

\[ \text{H} \Rightarrow \text{one bond and no lone pairs} \]

\[ \text{F, Cl, Br, and I} \Rightarrow \text{one bond and three lone pairs} \]

\[ \text{O, S, Se, and Te} \Rightarrow \text{two bonds and two lone pairs} \]

\[ \text{N, P, As, and Sb} \Rightarrow \text{three bonds and one lone pair} \]

\[ \text{C, Si, Sn, and Ge} \Rightarrow \text{four bonds and no lone pairs} \]

\[ \text{H} \quad \text{H} \]

\[ \text{H} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{S} \quad \text{H} \]

\[ \text{H} \quad \text{H} \]
Ask Students: For each of the following molecules, draw the correct Lewis Dot Structures including all Bonds and Lone Pairs

Group Activity

\[
\begin{align*}
&H \quad H \quad O \\
&H \quad C \quad C \quad C \quad C \quad C \quad C \quad H \\
&H \quad H \quad H \quad H \quad H
\end{align*}
\]

\[
\begin{align*}
&H \quad H \quad Cl \quad O \\
&H \quad C \quad C \quad C \quad O \quad C \quad H \\
&Cl \quad H \quad H
\end{align*}
\]

\[
\begin{align*}
&H \\
&H \quad H \quad Se \\
&H \quad C \quad C \quad O \quad N \quad C \quad H \\
&I \quad H \quad H \quad H
\end{align*}
\]
2E Waves of Light

- Graphics from Text: Figure 2.1, Wave Motion
- The relationship between Frequency, Wavelength, and Amplitude for Electromagnetic Waves

- Electromagnetic Spectrum

- Wavelength of Electromagnetic Waves
  - Long wavelengths correspond to low energy waves
  - Is inversely related to the Frequency of Electromagnetic Waves

- Wavelength = Speed of Light / Frequency
- \( \lambda = \frac{C}{\nu} \)
- \( C = \text{Speed of Light} = 3 \times 10^8 \text{ m/sec} \)
Frequency of Electromagnetic Waves

- High frequency corresponds to high energy waves
- Is inversely related to the Wavelength of Electromagnetic Waves

Frequency = Speed of Light / Wavelength

\[ \nu = \frac{C}{\lambda} \]

Amplitude of Electromagnetic Waves

- Is related to the intensity of the wave
Graphics from Text: Figure 2.2, the Electromagnetic Spectrum

The relationship between frequency and wavelength for various types of electromagnetic radiation

Graphics from Text: Figure 2.3, Solar Radiation Profile

The distribution of electromagnetic radiation of various energies produced by the sun as they appear from just above the earth’s atmosphere

Note: the Overall Profile (Black Body Radiation)

The Spikes and Valleys (Specific Absorptions by Materials between the eye and the sun.

Ask Students: As the temperature of the object changes, how will the shape of Figure 2.3 change?

Group Activity
Wave/Particle Duality

- Light is Wave Like
  - Evidence includes Diffraction
    - I.e., light bends

- Light is Particle Like
  - Evidence includes Photoelectric Effect
    - I.e., there is a threshold energy for light to cause its effects

- Wave / Particle Duality
  - Light has Both Wave and Particle Like Properties
    - Plank’s Relationship $E = h \nu$
      - $h$ is Plank’s Constant ($6.63 \times 10^{-34}$ joule seconds)
      - Higher Frequency $\Rightarrow$ Higher Energy
      - Lower Frequency $\Rightarrow$ Lower Energy
      - Wave Packet Model
2G The Ozone Screen

- Graphics from Text: Figure 2.4 (3rd Edition only), Atmospheric Sunscreen
- The atmosphere (and especially the Stratospheric Ozone Layer) acts as sunscreen to select out which wavelengths of light reach the earth’s surface

- Graphics from Text: Figure 2.4 in 2nd Edition and 2.5 in 3rd Edition, Atmosphere’s effect on solar radiation reaching the earth’s surface
- The atmosphere “screens” us from high energy UV light reaching the surface

- Graphics from Text: Figure 2.5 in 2nd Edition and 2.6 in 3rd Edition, Ozone’s Absorption of Ultra-Violet Radiation
- Ozone absorbs high energy UV light
Molecular reasons for these effects

- Molecular Oxygen, $O_2$, absorbs the highest energy UV light
  - UV light with $\lambda$ less than about 242 nm

\[ O_2 + \text{photon} \rightarrow 2\ O \]

- Ozone, $O_3$, absorbs the medium energy UV light
  - UV light with $\lambda$ less than about 320 nm (i.e., lower energy)
  - Ozone has a typical lifetime of about one or two hundred seconds
  - Ozone has a weaker O-O bond than molecular oxygen and this bond is therefore broken by lower energy photons

\[ O_3 + \text{photon} \rightarrow O_2 + O \]
Ozone Cycle

Ozone generation in the atmosphere

\[ O + O_2 \rightarrow O_3 \text{ (formation of ozone)} \]

Graphics from Text: Figure 2.7 in 2nd Edition and 2.11 in 3rd Edition, Ozone concentration profile of the atmosphere

Ozone concentrations are highest in the part of the stratosphere referred to as the Ozone Layer

Graphics from Text: Figure 2.6 in 2nd Edition and 2.10 in 3rd Edition, The Chapman Cycle of Ozone in the Atmosphere
❖ Ozone Destruction

❖ Free Radicals!!!

❖ Radicals are molecules or atoms with one or more unpaired electrons

❖ This makes them extremely reactive and they can catalyze reaction such as Ozone destruction

\[
\begin{align*}
H_2O + \text{energy} & \rightarrow H^\cdot + OH^\cdot \\
H^\cdot + O_3 & \rightarrow OH^\cdot + O_2 \\
OH^\cdot + O & \rightarrow H^\cdot + O_2 \\
\hline
H^\cdot + O_3 + OH^\cdot + O & \rightarrow OH^\cdot + O_2 + H^\cdot + O_2 \\
\end{align*}
\]

Net Reaction: \[ O + O_3 \rightarrow 2 O_2 \]
➢ Ozone Loss

➢ Arctic and Antarctic Sensitivity

➢ Caused by extreme cold ⇒ tiny crystals whose surfaces are involved in Ozone destruction

➢ Note: Noise levels in data

➢ Graphics from Text: Figure 2.8 in 2nd Edition and 2.7/2.12 in 3rd Edition, Average Ozone loss on the earth

➢ A few percent in continental US

➢ Graphics from Text: Figure 2.9 in 2nd Edition and 2.13 in 3rd Edition, Ozone loss in Antarctica

➢ About 50% in the high Antarctic
2H CFCs and Ozone

- Halocarbons
  - Compounds containing only C, Cl, F, Br, and H
  - Are typically expensive but safe
    - non-toxic, non-flammable, non-reactive, and quite volatile
  - Used as refrigerants, blowing agents, propellants, cleaning agents for computer parts, dry cleaning fluids, decaffination
Classes of Halocarbons

CFCs are Chlorofluorocarbons

- These are chemicals that contain only C, Cl, and F
- Examples include: CFCl₃ (Freon 11) and CF₂Cl₂ (Freon 12)

Halons contain C, Br, and F and/or Cl

- Examples include: CH₃Br, CF₂Br₂ and CClBr₃
- Used for fire extinguishers

Chlorocarbons contain C, Cl, and H

- Examples include CCl₃-CH₃ and CH₂Cl₂
Halocarbons and Ozone Destruction

They are generally safe at ground level, why are they dangerous in the Stratosphere?

They are so stable that unlike most chemicals they escape destruction in the decade or so it takes them to make it to the Stratosphere

This means that they can transfer Chlorine and Bromine atoms here much better than other chemicals

In the Stratosphere, these Cl and Br containing compounds produce Cl\(^+\) and Br\(^+\) radicals which catalyze Ozone destruction

Bromine radicals are much less concentrated but are much more destructive

The man made examples of halocarbons are typically more stable than the natural ones and therefore typically make it to the Stratosphere better
Reactions that destroy Ozone

\[ \text{CF}_2\text{Cl}_2 + \text{energy} \rightarrow \text{CF}_2\text{Cl}^\cdot + \cdot\text{Cl} \]

\[ \cdot\text{Cl}^\cdot + \text{O}_3 \rightarrow \cdot\text{OCl} + \text{O}_2 \]

\[ \cdot\text{OCl} + \text{O} \rightarrow \text{Cl}^\cdot + \text{O}_2 \]

\[ \text{Cl}^\cdot + \text{O}_3 + \cdot\text{OCl} + \text{O} \rightarrow \cdot\text{OCl} + \text{O}_2 + \cdot\text{Cl} + \text{O}_2 \]

Net Reaction: \[ \text{O} + \text{O}_3 \rightarrow 2\text{O}_2 \]

Note: this reaction is very similar to that for Ozone destruction by hydrogen radicals, it is just much faster and thus more efficient

The analogous reaction with bromine radicals is even faster and more efficient

Graphics from Text: Figure 2.11 in 2\textsuperscript{nd} Edition and 2.15 in 3\textsuperscript{rd} Edition, Chlorine - Ozone Correlations
➢ Solutions?

➢ Many now in place or being put into effect

➢ “Montreal Treaty”

➢ Cost Concerns

➢ Safety Concerns

➢ Technology Concerns

➢ Hydrochlorofluorocarbons

➢ Supercritical CO₂

➢ Greenhouse gasses
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<td>Wave/Particle Duality</td>
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<td>What is Ozone</td>
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<td>What is the Structure of a Atom</td>
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