Protecting the Ozone Layer

Properties of Ozone
- Triatomic oxygen gas or O₃
- “to smell” in Greek; odor at 10 ppb
- Lightning; welding; photocopying or electric motor sparking
- Energy + 3 O₂ → 2 O₃
- Water purification and bleaching of paper pulp and fabrics

Allotropes
- Two or more forms of the same element
- Differ in molecular structure
- Differ in properties
- Allotropic forms exist in oxygen, carbon, and phosphorus.

Comparison of Allotropes

<table>
<thead>
<tr>
<th></th>
<th>O₃</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point</td>
<td>-112°C</td>
<td>-183°C</td>
</tr>
<tr>
<td>Color of liquid</td>
<td>Dark blue</td>
<td>Light blue</td>
</tr>
<tr>
<td>Odor</td>
<td>Smelly</td>
<td>Odorless</td>
</tr>
</tbody>
</table>

Carbon Allotropes
- Diamond (tetrahedral units)
- Graphite (layers of hexagonal units)
- Buckyball (C₆₀ or C₇₀)
- Carbon nanotubes (cylindrical)

Tropospheric Ozone
- O₃ is formed in the troposphere via the reaction of volatile organic compounds and nitrogen oxides in the presence of sunlight.
- O₃ is commonly associated with smog in polluted urban areas.
- O₃ in troposphere is also called bad ozone because it causes respiratory illnesses including asthma.
Stratospheric Ozone

- Stratospheric ozone or the “good ozone” is found at high altitudes about 20-30 km above the Earth.
- The “good ozone” absorbs the harmful UV radiation from the Sun, thereby lessening the incidence of skin cancers.

Review: Pure Substances

- Elements are composed of distinctive and characteristic atoms that are indivisible by chemical means.
- Atoms can join together to form molecules, which are basic units of compounds.

Sub-atomic Particles

- > 200 known to date
- Nucleus (dense core)
  - Protons
  - Neutrons
- Electrons occupy diffuse region around nucleus.

Protons

- Positive (+) charge
- Attract electrons around nucleus by electrostatic forces
- Equivalent mass to neutron
- Contained in nucleus

Neutrons

- No charge or neutral
- Equivalent mass to proton
- Contained in nucleus
- Atoms of the same element may have different number of neutrons.

Electrons

- Negative (-) charge
- 1/2000 mass of proton
- Occupy various regions with unique shapes outside nucleus
- Consists of the outermost “reactive” valence electrons and the tightly held inner-core electrons.
- Rearrangement of electrons are involved in chemical reaction.
**Atomic Number**
- Periodic Table
- # of protons
- Neutral atom
- Identity of atom

**Table 2.1**

<table>
<thead>
<tr>
<th>Particle</th>
<th>Relative Charge</th>
<th>Relative Mass</th>
<th>Actual Mass, kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton</td>
<td>+1</td>
<td>1</td>
<td>$1.67 \times 10^{-27}$</td>
</tr>
<tr>
<td>Neutron</td>
<td>0</td>
<td>1</td>
<td>$1.67 \times 10^{-27}$</td>
</tr>
<tr>
<td>Electron</td>
<td>-1</td>
<td>1/1838 = 0.0005444</td>
<td>$9.11 \times 10^{-31}$</td>
</tr>
</tbody>
</table>

**Periodic Table**
- Increasing atomic number
- Chemical & physical properties
- Groups or families

**Electronic Arrangement**
- Number of outer electrons
- “valence electrons”
- “do” chemistry
- Table 2.2 page 50
Isotopes

- Two or more forms of the same element, (same number of protons) whose atoms differ in the number of neutrons

Mass Number

- Sum of protons and neutrons
- Specific atom
- Isotopes have different mass numbers
- 2.5 Your Turn, page 51

Molecular Structure

- Defines the material
- Identifies both chemical and physical properties
- Compounds with the same chemical formula may have different structures

Covalent Bond

- 2 shared electrons in a chemical bond
- Typically between 2 non-metals or non-metal and hydrogen
- Electron sharing helps achieve molecular stability via octet configuration.
Lewis Structure
- Rules on page 54: (1) Sum up all the valence electrons (2) Arrange electrons in bonding pairs and lone pairs or non-bonding pairs.
- Lewis structures usually have symmetry.
- Octet rule or configuration applies to many elements except for H, He, and B.

Types of Bonds
- Single (e.g. H₂O, CH₄, Cl₂)
- Double (e.g. CO₂, O₂)
- Triple (e.g. CO, N₂)
- Fractional (e.g. 1½ bond in O₃; usually in molecules with resonance structures)

Fig. 2.2 on Page 58

Wavelength
- Distance between successive peaks in an electromagnetic wave
- Units of length
- $\lambda$ (lambda)
- Small (nm) to very large (m)

Frequency
- Number of waves passing a fixed point in one second
  - Waves per second, 1/s
  - Hertz, Hz
  - $\nu$ (nu)

Relationships of $\nu$ and $\lambda$
- Wavelength is inversely proportional to frequency
- Frequency increases as wavelength decreases
- $\nu = \frac{c}{\lambda}$
- $c =$ speed of light and other radiation $= 3.00 \times 10^8$ m/s
Most of the energy of solar radiation is in the infrared spectral region even though the visible radiation has the highest intensity. UV, with only 8% of the total solar energy, is the most damaging biologically.

Solar Spectrum Above the Atmosphere

Properties of Photons

- Photons are particles of light carrying bundles of energy.
- Photons have no mass.
- Photon energy is described by the Planck’s Equation.

Planck’s Equation

- $E = h\nu = hc/\lambda$
- Equation applies for all forms of radiant energy
- Energy or frequency increases as wavelength decreases.
- Planck’s constant ($h$)
  - $h = 6.63 \times 10^{-34}$ Js
  - J is a small unit of energy.
UV and O₂
- \( O₂ + \text{photon} \rightarrow 2\, O \)
- \( \lambda \leq 242\, \text{nm} \) needed to break the double bond of O₂
- UV radiation is absorbed by O₂
- Shields Earth from harmful UV radiation from the sun

Ozone
- \( O₃ + \text{photon} \rightarrow O₂ + O \)
- \( \lambda \leq 320\, \text{nm}; 242–320\, \text{nm} \) absorbed mainly by O₃
- O₃ is more reactive than O₂ because its bond is weaker (1.5 bond versus double bond)
- Small amount of UV still reaches Earth

Biological Effects of UV
- Depends on the intensity of radiation and wavelength
- Sensitivity to radiation is related to the amount of energy per photon
- Energy on surface drops due to O₃ and O₃
Biological Effects of Photons

- Excite electrons to higher energy levels
- Break bonds biomolecules such as DNA (deoxyribonucleic acids)
- Alter molecular properties or cause gene mutations in the p53 gene of cancerous skin cells

Biological Sensitivity

- Damage to DNA
- Measured at specific $\lambda$
- Decreasing $\lambda$
- Increasing energy
- Increasing DNA damage

Figure 2.10 on Page 63

UV Index

- Table 2.3 page 65
- UV-A, 320-400 nm
- UV-B, 280-320 nm
- UV-C, $\leq 280$ nm

Ozone Layer

- Removes all UV-C
- Removes most UV-B
- Does not affect UV-A
**UV-B**
- Damages DNA and induces mutation in p53 gene in skin cells
- Causes skin cancers/melanoma
- Weakens immune system
- Causes snow blindness or eye damage leading to cataracts
- Harm crops and marine organisms

**UV-A**
- UV-A is not absorbed by O₂ or O₃ due to its lower energy.
- UV-A is suspected of causing premature wrinkling and aging.
- Skin cancers may also be due to UV-A.

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**Table 2.5**

<table>
<thead>
<tr>
<th>Radiation</th>
<th>Wavelength Range</th>
<th>Energy</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-A</td>
<td>320–400 nm</td>
<td>Least energetic of these three UV categories</td>
<td>Least damaging, reaches Earth’s surface in greatest amount</td>
</tr>
<tr>
<td>UV-B</td>
<td>280–320 nm</td>
<td>More energetic than UV-A, less energetic than UV-C</td>
<td>More damaging than UV-A, less damaging than UV-C, most absorbed by ozone in the stratosphere</td>
</tr>
<tr>
<td>UV-C</td>
<td>200–280 nm</td>
<td>Most energetic of these three categories</td>
<td>Most damaging of these three, but not a problem because totally absorbed by oxygen and ozone in stratosphere</td>
</tr>
</tbody>
</table>

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**Figure 2.11 on Page 64**

Southwestern U.S. has a higher incidence of skin cancers that is correlated with higher solar UV radiation.

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**Tanning: Risk or Benefit**
- UV-B in solar radiation or tanning bed increases risk of skin cancer; over 1,000,000 new cases per year.
- Vermont has the highest melanoma skin cancer rate; outdoor sports or tanning salons as causes?
- Sunscreen with Skin Protection Factors or SPF of 15 or greater should be used.

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Blacks are more susceptible than whites to melanoma skin cancers
Sunscreen Lotion

- Fair-haired and fair-skinned people are at the highest risk to develop skin cancer from UV-B radiation (e.g. Australian).
- American Academy of Dermatology recommends sunscreens with SPF of 15-30
- The use of sunscreen does not prevent skin cancer

Stratospheric Ozone

- 300,000,000 tons $O_3$ are formed and destroyed each day in a dynamic steady state
- The equilibrium concentration of ozone depends on UV intensity, $O_2$ concentration, and altitude.

Chapman Cycle (1929)

- Cycle of chemical reactions explaining the steady state of $O_3$
- Figure 2.14 page 71

O$_3$ in the Atmosphere

- How is $O_3$ measured?
  - Ground-based UV detectors (1930-)
  - Satellites-mounted detectors (1970-)
  - Airplanes, rockets, and balloons.
- Ozone concentration varies as a function of altitudes and is highest at 20 km; 91% of ozone is in the stratosphere of 10-50 km; fragile ozone shield of 0.30 cm thick at 1.0 atm and 15 °C.

Stratospheric $O_3$ Destruction

- Over 80 years of ozone data
- Actual concentration is less than predicted by Chapman
- Concentration is not uniform; ~320 DU at the Artic and ~250 DU near the equator (1 DU ~ 1 ppb)
- Area with less than 220 DU is defined as the ozone hole.
Ozone Concentration

- $O_3$ levels increase from the Equator toward the Poles.
- Varies with seasons and correlated with solar UV radiation intensity; maximum in March, minimum in October for the northern hemisphere.
- Sunspot activity (11-12 years)
- Winds (28-month cycles)

Natural Destruction of $O_3$

- Free radicals deplete $O_3$
- Unstable chemical species with an unpaired electron
- $H_2O + UV \rightarrow H+ OH$
- Radical + $O_3 \rightarrow O_2 + R.O$

Ozone Destruction by Radicals

- $N_2O + O \rightarrow 2 NO$
- $N_2O$ from microorganisms
- Supersonic transport planes
- Energy + $N_2 + O_2 \rightarrow 2 NO$
- Natural destruction alone does not explain why $O_3$ concentrations lower than predicted.

Ozone Concentrations in Arosa, Switzerland

- The decrease of ozone ($60^\circ$N- $60^\circ$S) by 6% between 1979 and 1995 is correlated with an increase in skin cancers.
• The decline from average ozone concentrations over Antarctica during spring is more drastic than that during summer.
• Polar stratospheric clouds convert ClONO₂ and HCl to HOCl and Cl₂, capable of releasing Cl atoms for ozone depletion.

**Discovery of Ozone Hole**
- Rowland, Molina, and Crutzen shared 1995 Nobel Prize
- Analyzed atmospheric data and identified chlorofluorocarbons (CFCs) as the main culprits in ozone depletion.
- CFCs are man-made as opposed to natural OH• and NO• radicals

**CFCs**
- Contains halogens (F and Cl), Group 17 or Group VIIA
- Fluorine, F
- Chlorine, Cl
- And Carbon, C

**Group VIIA (17) Halogens**
- All three are diatomic molecules including fluorine.
- Fluorine, F, most reactive element; Teflon
- Chlorine, Cl is used as disinfectant in water purification, starting material
- Bromine, Br is present in flame retardant formulation

**Group 17 Elements**
- Used in many materials
CFCs
- Synthetic, DuPont
- CF₂Cl₂; CFC-12
- CFCl₃; CFC-11
- “Freons”
- Refrigerants

CFCs
- Propellants
- Gases for foams
- Solvents
- With Br, fire fighting foams

CFCs as Refrigerants
- Replaced toxic ammonia, NH₃, and sulfur dioxide, SO₂
- Inert
- Non-toxic
- Does not burn
- Inexpensive

More CFCs
- Air conditioning
- Boom in the south
- Economy changed
- 850,000 tons in 1985

Why a problem?
- Strong C-Cl and C-F bonds
- Can persist for 120 years or more in atmosphere
- UV-C can break C-Cl bonds
- 1973, Rowland and Molina

Problem cont.
- CCl₂F₂ + photon → CCIF₂ + Cl
- λ ≤ 220 nm
- Free radicals are very reactive!
More

- $2 \cdot \text{Cl} + 2 \text{O}_3 \rightarrow 2 \cdot \text{ClO} + 2 \text{O}_2$
- $\text{ClO} + \cdot \text{ClO} \rightarrow \text{ClO-OCIO}$
- $\text{ClO-OCIO} + \text{UV} \rightarrow \cdot \text{ClOO} + \cdot \text{Cl}$
- $\cdot \text{ClOO} + \text{UV} \rightarrow \cdot \text{Cl} + \text{O}_2$

Net Equation

- $2 \text{O}_3 \rightarrow 3 \text{O}_2$
- Atomic chlorine, $\cdot \text{Cl}$
- Destroys $\text{O}_3$
- Maximum destruction occurs above 30 km

Chlorine as a Catalyst

- $\cdot \text{Cl}$ is both reactant and product
- Regenerated in reactions
- Catalytic role of $\cdot \text{Cl}$
- Destroys 100,000 ozone molecules per chlorine atom

Antarctic Ozone Hole

- The South Pole is the coldest place on Earth
- Clouds of ice crystals allows surface chemistry
- Ozone hole is formed during Antarctic spring (September – November)
- Causes crop damage and skin cancers

Artic Ozone Hole?

- Occurs in March-April (spring)
- $\text{ClO}$ has been detected but the less colder climate help moderate the ozone depletion.
- Harmful effects are more significant due to the larger population north of 60°N latitude.
What is being done?
- 82% of stratospheric Cl comes from synthetic chemicals like CFCs.
- Banned spray cans in 1978
- Banned foaming agents in 1990
- Ozone depletion is a global problem requires international cooperation

Protection of Ozone Layer
- 1985- Vienna Convention on the Protection of Ozone Layer
- 1987- Montreal Protocol on Substances That Deplete the Ozone Layer
- Reduce production of CFCs to 50% of 1986 levels by 1998

Fig. 2.23 on Page 86

More global regulations
- Ban production of CFCs by 2000
- Halons (C-F-Br compounds) and CCl₄ to be phased out by 2010; developing nations to stop using CH₃Br (agricultural fumigant) by 2015
- Copehagen Amendments ban the production of HCFCs by 2030

CFCs
- Legal but expensive
- Favorite of smugglers
- High tax
- Still manufactured in Mexico, China, and Russia

Page 74; Table 2.4

<table>
<thead>
<tr>
<th>Table 2.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two Important Hydrochlorofluorocarbons</td>
</tr>
<tr>
<td>HCFC-22</td>
</tr>
<tr>
<td>CHClF₂</td>
</tr>
<tr>
<td>Chlorodifluoromethane</td>
</tr>
<tr>
<td>H–Cl–F</td>
</tr>
<tr>
<td>H–C–F</td>
</tr>
<tr>
<td>H–Cl</td>
</tr>
</tbody>
</table>

The lifetime of HCFC-22 is 20 years compared to 111 years for CFC-12 and its ozone depletion potential is only 5% of that for CFC-12.
CFC Substitutes

- HCFC-22 (CHF₂Cl) & HCFC-141b (C₂H₃FCl₂)
- HFC-134a (CF₃CH₂F)
- Propane (C₃H₈) & isobutane (C₄H₁₀)
- Must meet the requirements of toxicity, flammability, and stability; boiling point of −10 to −30 °C.

Pyrocool FEF, a foam designed to replace halons used in fire fighting, won the 1998 Presidential Green Chemistry Award.