ANSWERS TO END-OF-CHAPTER QUESTIONS

CHAPTER 2: PROTECTING THE OZONE LAYER

Emphasizing Essentials

1. How does ozone differ from oxygen in its chemical formula? In its properties?

Answer:
The chemical formulas of ozone and oxygen are O_3 and O_2, respectively. Both are gases, but they differ in their properties. Oxygen has no odor; ozone has a very sharp odor. Although both are reactive, ozone is much more highly so. Oxygen is necessary for many forms of life; in contrast, ozone is a harmful air pollutant in the troposphere. However, ozone in the stratosphere helps to protect us from the harmful ultraviolet rays of the sun.

2. Explain why is it possible to detect the pungent odor of ozone after a lightning storm or around electrical transformers.

Answer:
Energy from lightning or from an electrical arc associated with a transformer can cause oxygen molecules in the air to split to form oxygen atoms. These oxygen atoms then react with oxygen molecules to produce ozone. The overall chemical change is:

$$\text{Energy} + 3\ O_2 \rightarrow 2\ O_3$$

3. The text states that the odor of ozone can be detected in concentrations as low as 10 ppb. Will you be able to detect the odor of ozone in either of these air samples?
a. 0.118-ppm ozone, a concentration reached in the troposphere
b. 25-ppm ozone, a concentration reached in the stratosphere

Answer:
a. Yes, this is over the detection minimum of 10 ppb.

$$\frac{0.118\ \text{parts O}_3}{1{,}000{,}000\ \text{parts air}} = \frac{118\ \text{parts O}_3}{1{,}000{,}000{,}000\ \text{parts air}}\ \text{or 118 ppb}$$

b. Yes, this is well over the detection minimum of 10 ppb.

$$\frac{25\ \text{parts O}_3}{1{,}000{,}000\ \text{parts air}} = \frac{25{,}000\ \text{parts O}_3}{1{,}000{,}000{,}000\ \text{parts air}}\ \text{or 25,000 ppb}$$

4. A journalist wrote "Hovering 10 miles above the South Pole is a sprawling patch of stratosphere with disturbingly low levels of radiation-absorbing ozone."
a. How big is this sprawling patch?
b. Is the figure of 10 miles correct? Express this value in kilometers.
c. What type of radiation does ozone absorb?

Answer:

a. The size of the ozone "hole" varies each year, but has been estimated to be as large as 28 million km^2 in area.

b. $10 \text{ miles} \times \dfrac{\text{km}}{0.621 \text{ miles}} = 16.1 \text{ km}$

Yes, the figure is correct, as the stratosphere extends between 15 and 30 km above the Earth's surface.

c. Ozone absorbs UV-B and UV-C radiation.

5. It has been suggested that the term *ozone screen* would be a better descriptor than *ozone layer* to describe ozone in the stratosphere. What are the advantages and disadvantages to each term?

Answer:

The term *ozone layer*, while in widespread use, brings to mind an incorrect image of a blanket-like layer. In fact, even in the stratospheric region of highest concentration, ozone's concentration is typically less than 1 ppm and is not even the most abundant species in that region. The ozone does not completely block all UV radiation, such as a blanket might block all visible light. The ozone that is present, however, serves the essential function of absorbing some wavelengths of UV-B, reducing its intensity before it reaches the surface of the Earth, making the screen analogy more useful.

6. Assume there are 2×10^{20} CO molecules per cubic meter in a sample of tropospheric air. Furthermore, assume there are 1×10^{19} O_3 molecules per cubic meter at the point of maximum concentration of the ozone layer in the stratosphere.

a. Which cubic meter of air contains the larger number of molecules?

b. What is the ratio of CO to O_3 molecules in a cubic meter?

Answer:

a. The air containing 2×10^{20} molecules of CO

b. $\dfrac{2 \times 10^{20}}{1 \times 10^{19}} = 20$; The ratio is 20:1

7. **a.** What is a Dobson unit?

b. Does a reading of 320 DU or 275 DU indicate more total column ozone overhead?

Answer:

a. The Dobson unit (or DU) measures the ozone in a column above a specific location on Earth. If this ozone were compressed at specified conditions of temperature and pressure, it would form a layer. A layer 3 mm thick corresponds to 300 DU. Similarly, a 1 mm layer corresponds to 100 DU.

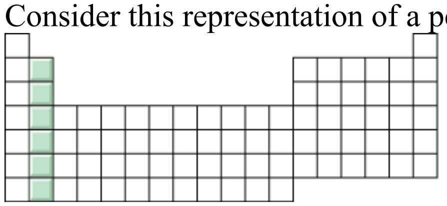
b. 320 DU > 275 DU Thus, 320 DU indicates more total ozone overhead.

8. Using the periodic table as a guide, specify the number of protons and electrons in a neutral atom of each of these elements.

a. oxygen (O)
b. nitrogen (N)
c. magnesium (Mg)
d. sulfur (S)

Answer:
a. A neutral atom of oxygen has 8 protons and 8 electrons.
b. A neutral atom of nitrogen has 7 protons and 7 electrons.
c. A neutral atom of magnesium has 12 protons and 12 electrons
d. A neutral atom of sulfur has 16 protons and 16 electrons

9. Consider this representation of a periodic table:



a. What is the group number of the shaded column?
b. Which elements make up this group?
c. What is the number of electrons for a neutral atom of each element in this group?
d. What is the number of outer electrons for a neutral atom of each element of this group?

Answer:
a. Group 2A
b. beryllium, Be; magnesium, Mg; calcium, Ca; strontium, Sr; barium, Ba; radium, Ra
c. Be 4, Mg 12, Ca 20, Sr 38, Ba 56, Ra 88.
d. Each element in Group 2A has 2 outer electrons.

10. Give the name and symbol for the element with this number of protons.
a. 2
b. 19
c. 29

Answer:
a. helium, He
b. potassium, K
c. copper, Cu

11. Give the number of protons, neutrons, and electrons in each of these neutral atoms.
a. oxygen-18 ($^{18}_{8}O$)
b. sulfur-35 ($^{35}_{16}S$)
c. uranium-238 ($^{238}_{92}U$)
d. bromine-82 ($^{82}_{35}Br$)
e. neon-19 ($^{19}_{10}Ne$)
f. radium-226 ($^{226}_{88}Ra$)

Answer:

a. 8 protons, 10 neutrons, 8 electrons
b. 16 protons, 19 neutrons, 16 electrons
c. 92 protons, 146 neutrons, and 92 electrons
d. 35 protons, 47 neutrons, 35 electrons
e. 10 protons, 9 neutrons, 10 electrons
f. 88 protons, 138 neutrons, and 88 electrons

12. Give the symbol showing the atomic number and the mass number for the isotope that has:
a. 9 protons and 10 neutrons (used in nuclear medicine).
b. 26 protons and 30 neutrons (the most stable isotope of this element).
c. 86 protons and 136 neutrons (the radioactive gas found in some homes).

Answer:

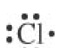
a. $^{19}_{9}\text{F}$
b. $^{56}_{26}\text{Fe}$
c. $^{222}_{86}\text{Rn}$

13. Draw the Lewis structure for each of these atoms.
a. calcium
b. nitrogen
c. chlorine
d. helium

Answer:

a. 

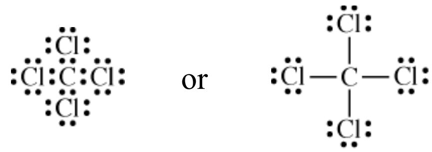
b. 

c. 

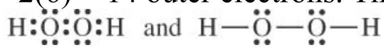
d. 

14. Assuming that the octet rule applies, draw the Lewis structure for each of these molecules.
a. CCl_4 (carbon tetrachloride, a substance formerly used as a cleaning agent)
b. H_2O_2 (hydrogen peroxide, a mild disinfectant;
the atoms are bonded in this order: H–O–O–H)
c. H_2S (hydrogen sulfide, a gas with the unpleasant odor of rotten eggs)
d. N_2 (nitrogen gas, the major component of the atmosphere)
e. HCN (hydrogen cyanide, a molecule found in space and a poisonous gas)
f. N_2O (nitrous oxide, "laughing gas"; the atoms are bonded N–N–O)
g. CS_2 (carbon disulfide, used to kill rodents; the atoms are bonded S–C–S)

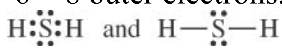
Answer:

a. There are 4 + 4(7) = 32 outer electrons 

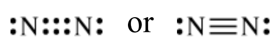
b. There are 2(1) + 2(6) = 14 outer electrons. The Lewis structure is:



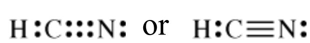
c. There are 2(1) + 6 = 8 outer electrons. The Lewis structure is:



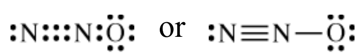
d. There are 2(5) = 10 outer electrons. The Lewis structure is:



e. There are 1 + 4 + 5 = 10 outer electrons. The Lewis structure is:

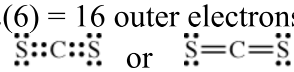


f. There are 2(5) + 6 = 16 outer electrons. One possible Lewis structure is:



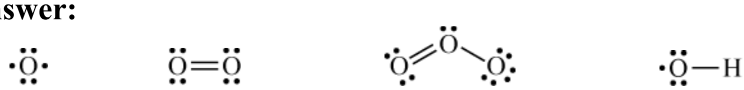
Other resonance structures are possible for N^2O as well.

g. There are 4 + 2(6) = 16 outer electrons. The Lewis structure is:



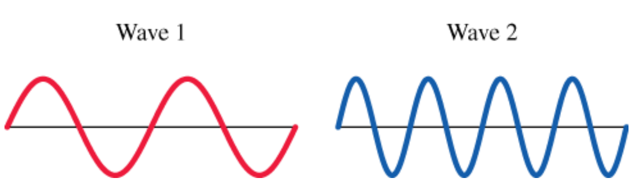
15. Several oxygen species play important chemical roles in the stratosphere, including oxygen atoms, oxygen molecules, ozone molecules, and hydroxyl radicals. Draw Lewis structures for each.

Answer:



The Lewis structures for the oxygen molecule and the ozone molecule both follow the octet rule. In contrast, the oxygen atom has only 6 outer electrons and does not follow the octet rule. The hydroxyl radical also does not follow the octet rule and has an unpaired electron. Another resonance structure for the ozone molecule may be drawn; the other molecules do not have resonance structures.

16. Consider these two waves representing different parts of the electromagnetic spectrum. How do they compare in terms of:



a. wavelength
b. frequency
c. speed of travel

Answer:

a. Wave 1 has longer wavelength than wave 2.
b. Wave 1 has lower frequency than wave 2.
c. Both waves travel at the same speed.

17. Use Figure 2.7 to specify the region of the electromagnetic spectrum where radiation of each wavelength is found. *Hint:* Change each wavelength to meters before making the comparison.
a. 2.0 cm
b. 400 nm
c. 50 mm
d. 150 mm

Answer:

a. $2.0 \text{ cm} \times \frac{1 \text{ m}}{10^2 \text{ cm}} = 2 \times 10^{-2} \text{ m}$ This wavelength is in the microwave region of the spectrum.

b. $400 \text{ nm} \times \frac{1 \text{m}}{10^9 \text{ nm}} = 4 \times 10^{-7} \text{ m}$ This wavelength is in the range of violet light in the visible region.

c. $50 \ \mu\text{m} \times \frac{1 \text{ m}}{10^6 \ \mu\text{m}} = 5 \times 10^{-5} \text{ m}$ This wavelength is in the infrared region of the spectrum.

d. $150 \text{ mm} \times \frac{1 \text{m}}{10^3 \text{mm}} = 1.5 \times 10^{-1} \text{ m}$ This wavelength is in the UHF/microwave region of the spectrum.

18. Arrange the wavelengths in question 17 in order of *increasing* energy. Which wavelength possesses the most energetic photons?

Answer:

$c = \nu \cdot \lambda$ and $\nu = \frac{c}{\lambda}$; c = 3.0 × 10^8 m·s^{-1} and E = h·ν and h = 6.63×10^{-34} J·s

a. $\nu = \frac{3.0 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{2 \times 10^{-2} \text{ m}} = 1.5 \times 10^{10} \text{s}^{-1}$ $E = (6.63 \times 10^{-34} \text{ J·s})(1.5 \times 10^{10} \text{ s}^{-1}) = 1.0 \times 10^{-24} \text{ J}$

b. $\nu = \frac{3.0 \times 10^8 \text{m} \cdot \text{s}^{-1}}{4 \times 10^{-7} \text{ m}} = 8 \times 10^{14} \text{ s}^{-1}$ $E = (6.63 \times 10^{-34} \text{ J·s})(8 \times 10^{14} \text{ s}^{-1}) = 5 \times 10^{-19} \text{ J}$

c. $\nu = \frac{3.0 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{5 \times 10^{-5} \text{ m}} = 6 \times 10^{12} \text{ s}^{-1}$ $E = (6.63 \times 10^{-34} \text{ J·s})(6 \times 10^{12} \text{ s}^{-1}) = 4 \times 10^{-21} \text{ J}$

d. $\nu = \frac{3.0 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{1.5 \times 10^{-1} \text{ m}} = 2.0 \times 10^9 \text{ s}^{-1}$ $E = (6.63 \times 10^{-34} \text{ J·s})(2.0 \times 10^9 \text{ s}^{-1}) = 1.3 \times 10^{-24} \text{ J}$

The most energetic photon corresponds to the shortest wavelength, 400 nm.

19. Arrange these types of radiation in order of *increasing* energy per photon: gamma rays, infrared radiation, radio waves, visible light.

Answer:

In order of increasing energy per photon: radiowaves < infrared < visible < gamma rays

20. The microwaves in home microwave ovens have a frequency of $2.45 \times 10^9\ s^{-1}$. Is this radiation more or less energetic than radio waves? Than X-rays?

Answer:

$c = v \cdot \lambda$ and $\lambda = \frac{c}{v}$; $c = 3.0 \times 10^8$ m/s

$$\lambda = \frac{3.0 \times 10^8\ m/s}{2.45 \times 10^9\ /s} = 1.2 \times 10^{-1}\ m$$

21. Ultraviolet radiation is categorized as UV-A, UV-B, or UV-C. Arrange these types in order of increasing:

a. wavelength
b. energy
c. potential for biological damage

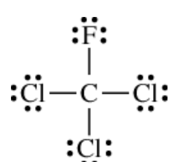
Answer:

a. In order of increasing wavelength: UV-C < UV-B < UV-A
b. In order of increasing energy: UV-A < UV-B < UV-C
c. In order of increasing potential for biological damage: UV-A < UV-B < UV-C

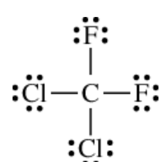
22. Draw Lewis structures for any three different CFCs.

Answer:

To qualify as CFCs, the compounds must contain only carbon, chlorine, and fluorine. Possibilities include:



CCl_3F
trichlorofluoromethane
Freon-11



CCl_2F_2
dichlorodifluoromethane
Freon-12

23. CFCs were used in hair sprays, refrigerators, air conditioners, and plastic foams. Which properties of CFCs made them desirable for these uses?

Answer:

All of these make use of the fact that CFCs are inert non-toxic gases that do not burn. Hair sprays, refrigerators, and air conditioners also make use of property that their boiling points are in a range useful for a refrigerant gas or propellant.

24. a. Can a molecule that contains hydrogen be classified as a CFC?

b. What is the difference between an HCFC and an HFC?

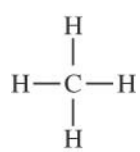
Answer:

a. No, a CFC molecule can contain only chlorine, fluorine, and carbon atoms.
b. HCFC molecules must contain hydrogen, carbon, fluorine, and chlorine atoms, and no other atoms In order for a molecule to be classified at an HFC, it must contain hydrogen, fluorine, and carbon (but no other atoms).

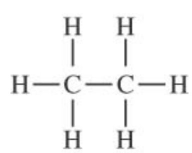
25. **a.** Most CFCs are based either on methane, CH_4, or ethane, C_2H_6. Use structural formulas to represent these two compounds.
b. Substituting chlorine atoms, fluorine atoms, or both for all of the hydrogen atoms on a methane molecule, you obtain CFCs. How many possibilities exist?
c. Which of the substituted CFC compounds in part **b** has been the most successful?
d. Why weren't all of these compounds equally successful?

Answer:

a. Methane, CH_4, has 4 + 4(1) = 8 outer electrons.



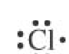
Ethane, C_2H_6, has 2(4) + 6(1) = 14 outer electrons.

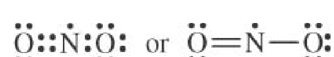


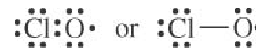
b. Three different CFCs are based on methane. They are: CF_3Cl, CCl_3F, and CCl_2F_2.
c. The most successful CFCs were $CFCl_3$ and CF_2Cl_2. These Freon® compounds were widely used in the U.S. as refrigerant gases.
d. Although many compounds are synthesized and tested for appropriate properties, only a few have the boiling points to serve as refrigerant gases.

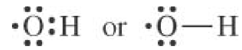
26. These free radicals all play a role in catalyzing ozone depletion reactions: Cl•, $•NO_2$, ClO•, and •OH.
a. Count the number of outer electrons available and then draw a Lewis structure for each free radical.
b. What characteristic is shared by these free radicals that makes them so reactive?

Answer:

a. Cl• has 7 outer electrons. Its Lewis structure is: 

$•NO_2$ has 5 + 2(6) = 17 outer electrons. Its Lewis structure is: 

ClO• has 7 + 6 = 13 outer electrons. Its Lewis structure is: 

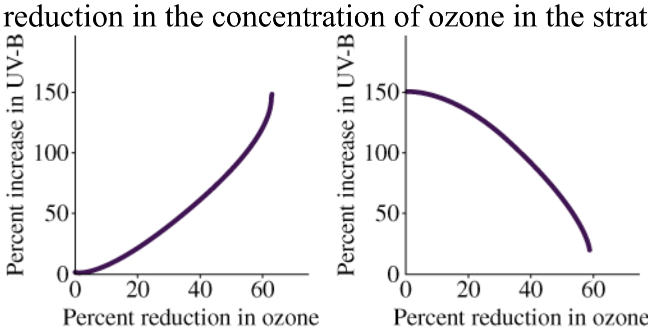
•OH has 6 + 1 = 7 outer electrons. Its Lewis structure is: 

b. They all contain an unpaired electron.

27. a. How were the original measurements of increases in chlorine monoxide and the stratospheric ozone depletion over the Antarctic obtained?
b. How are these measurements made today?

Answer:
a. The original measurements were obtained during flights of NASA's ER-2 research airplanes carrying measuring instruments over the Antarctic region.
b. Today these measurements are usually gathered via instruments in satellites.

28. Which graph shows how measured increases in UV-B radiation correlate with percent reduction in the concentration of ozone in the stratosphere over the South Pole?



(a) **(b)**

Answer:
The first graph is a more realistic representation of the relationship between the percent *reduction* in the concentration of ozone and the percent *increase* in UV-B radiation. As the ozone layer is depleted, the concentration of UV-B that can penetrate into the atmosphere rises. The second graph shows a type of inverse relationship, which is not substantiated by experimental facts.

Concentrating on Concepts

29. The EPA has used the slogan "*Ozone: Good Up High, Bad Nearby*" in some of its publications for the general public. Explain the message.

Answer:
The message is that ground-level ozone is a harmful air pollutant. Ozone in the stratosphere, on the other hand, is beneficial because it can absorb harmful UV-B before it reaches the surface of the Earth.

30. Nobel laureate F. Sherwood Rowland referred to the ozone layer as the Achilles heel of our atmosphere. Explain the metaphor.

Answer:

According to legend, Achilles was a man of mighty strength with one weak point - the heel of his foot. As the story goes, his downfall was caused by an arrow, possibly poisoned, shot to his heel. Similarly, our planet is robust and has great strengths. But it has a weak point – its atmosphere. If you damage the atmosphere, you may cause the downfall of the planet.

31. In the abstract of a talk he gave in 2007, Nobel laureate F. Sherwood Rowland wrote "Solar UV radiation creates an ozone layer in the atmosphere which in turn completely absorbs the most energetic fraction of this radiation."

a. What is the most energetic fraction? *Hint*: See Figure 2.8.

b. How does solar UV radiation "create an ozone layer"?

Answer:

a. The most energetic fraction is the UV light.

b. Up in the stratosphere where the air is very thin, UV-C splits oxygen molecules, O_2, into two oxygen atoms, O. These in turn react with other oxygen molecules to produce ozone, O_3. See the reactions of the Chapman Cycle. Without the UV-C light (which does not reach the surface of our planet), the ozone layer would not form.

32. In the conclusion of this chapter, we reported the words that Georgios Souflias spoke at the Symposium for the 20th Anniversary of the Montreal Protocol: "*We all, breathing on this planet today and having the potential, must guarantee its future, rapidly and decisively. We have no right to delay; we have no luxury of losing time.*"

a. What danger in delaying was he referring to?

b. Look back at the definitions of sustainability in the prologue. How do his words connect to these definitions?

Answer:

a. The danger is that if CFCs continue to accumulate, the damage of the ozone layer will continue not only in this generation, but to future ones (because of the long atmospheric lifetimes of the CFCs).

b. The definitions of sustainability all connect to making wise choices today, not only for our own health, but for that of those who live tomorrow. Souflias clearly speaks that we need to act on behalf of future generations as well as our own.

33. Consider the Chapman cycle in Figure 2.10.

a. Explain the source of the oxygen atoms.

b. Can this cycle take place in the troposphere as well? Explain.

Answer:

The Chapman cycle requires UV-C to break an oxygen molecule into two oxygen atoms. UV-C, however, does not reach the troposphere. This is one reason why the Chapman cycle cannot take place in the troposphere.

34. What are some of the reasons that the solution to ozone depletion proposed in this Sydney Harris cartoon will not work?

Source: Reprinted with permission, http://www.ScienceCartoonsPlus.com

Answer:

The solution proposed in the cartoon will not work for several reasons. One is that the amount of ozone required is too large to ship up to the stratosphere (and of course we don't have a series of freight planes heading up there anyhow). More importantly, if the mechanism for ozone destruction remains in place, any new ozone will be destroyed as well.

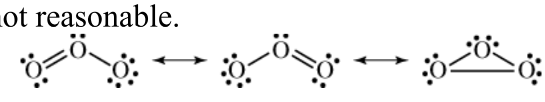
35. "*We risk solving one global environmental problem while possibly exacerbating another unless other alternatives can be found.*" The date of this quote by a U.S. official is 2009, and the context is phasing out the use of HCFCs.

a. What compounds were HCFCs being replaced in 2009?
b. What is the risk of this replacement?

Answer:

a. HFCs were being used to replace HCFCs.
b. HFCs are greenhouse gases!

36. It is possible to write three resonance structures for ozone, not just the two shown in the text. Verify that all three structures satisfy the octet rule and offer an explanation of why the triangular structure is not reasonable.

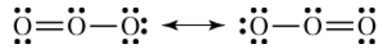


Answer:

Each Lewis structure has $3 \times 6 = 18$ electrons, and each oxygen atom has an octet of electrons. The triangular structure is not reasonable because the bond angles (60°) are much smaller than the usual bond angles.

37. The average length of an O–O single bond is 132 pm. The average length of an O–O double bond is 121 pm. What do you predict the O–O bond lengths will be in ozone? Will they all be the same? Explain your predictions.

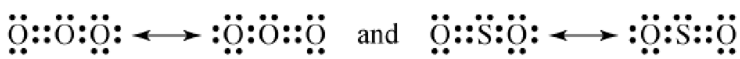
Answer:

Here are the resonance structures for ozone: 
Both contain 1 double bond (expected length of 121 pm) and 1 single bond (expected length of 132 pm). But in reality, the bonds are neither single nor double. Rather, the length of each bond is intermediate between the single and double bond lengths. A reasonable prediction would be 126 or 127 pm for both O–O bonds, midway between the two lengths.

38. Consider the Lewis structures for SO_2. How do they compare with the Lewis structures for ozone?

Answer:

With respect to valence electron distribution, the Lewis structures of SO_2 and ozone are identical. This should not be surprising, as sulfur and oxygen are in the same group on the periodic table, and thus have the same number of outer electrons. However, the atoms present in the two Lewis structures differ:



39. Even if you have skin with little pigment, you cannot get a tan from standing in front of a radio. Why?

Answer:

The energy of a photon of a radio wave is only about one ten-millionth of the energy of a photon of UV radiation. While UV radiation has sufficient energy to interact with melanin in skin pigments, radio waves do not.

40. The morning newspaper reports a UV Index Forecast of 6.5. Given the amount of pigment in your skin, how might this affect how you plan your daily activities?

Answer:

The UV Index, typically a number between 1 and 15, helps people to gauge how intense the sunlight is predicted to be on a particular day. A value of 6.5 (color-coded orange) indicates that there is high risk of harm and that you should protect your eyes and skin. A value of 8-10 indicates a very high risk and above 11 is an extreme risk.

41. All the reports of the damage caused by UV radiation focus on UV-A and UV-B radiation. Why is there no attention on the damaging effects of UV-C radiation?

Answer:

Although UV-C radiation causes damage to both animals and plants, it is completely absorbed by the O_2 in our atmosphere before it can reach the surface of the Earth.

42. If all 3×10^8 tons of stratospheric ozone that are formed every day are also destroyed every day, how is it possible for stratospheric ozone to offer any protection from UV radiation?

Answer:

Stratospheric ozone is both formed and broken down in a dynamic system called the Chapman Cycle. Unless there are disturbances to this system, the system remains in balance and there is no net change in the concentration of stratospheric ozone.

43. How does the chemical inertness of CCl_2F_2 (Freon-12) relate both the usefulness and the problems associated with this compound?

Answer:

See the answer to question #23. These compounds are useful because they are colorless, odorless, tasteless and generally inert. However, compounds such as these have long atmospheric lifetimes. They persist in the environment and make their way up to the stratosphere where they cause harm to the ozone layer.

44. Explain how the small changes in $ClO\cdot$ concentrations (measured in parts per billion) can cause the much larger changes in O_3 concentrations (measured in parts per million).

Answer:

$ClO\cdot$ acts as a catalyst in the series of reactions in which stratospheric O_3 molecules are changed to O_2 molecules. As it is not consumed in the reaction, $ClO\cdot$ can continue to catalyze the breakdown of O_3.

45. Development of the stratospheric ozone hole has been most dramatic over Antarctica. What set of conditions exist over Antarctica that help to explain why this area is well-suited to studying changes in stratospheric ozone concentration? Are these same conditions not operating in the Arctic? Explain.

Answer:

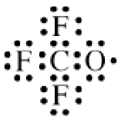
There are wide seasonal fluctuations in the temperatures and wind patterns in Antarctica. Development of polar stratospheric clouds of ice crystals during the long, dark, and still winter months provides reaction sites for the conversion of non-ozone depleting particles to reactive species. When the sun appears in Antarctica in late September and early October, the UV radiation releases $Cl\cdot$ from CFCs, initiating the destruction of ozone. The depletion in the Northern Hemisphere is not as severe as in the Southern Hemisphere. Scientists have not classified the ozone depletion over the North Pole as a "hole." The main reason for the observed difference between the total ozone changes in the two hemispheres is that the atmosphere above the North Pole usually is not as cold. Although polar stratospheric clouds have been observed in the Arctic (Figure 2.18), the air trapped over the Arctic generally begins to diffuse out of the region before the Sun gets bright enough to trigger as much ozone destruction as has been observed in Antarctica.

46. The free radical CF_3O? is produced during the decomposition of HFC-134a.

a. Propose a Lewis structure for this free radical.

b. Offer a possible reason why CF_3O? does not cause ozone depletion.

Answer:



a. There are 4 + 3(7) + 6 = 31 outer electrons available.
b. This free radical is very reactive in the troposphere, so it does not last long enough to reach the stratosphere.

47. One of the mechanisms that helps to break down ozone in the Antarctic region involves the BrO• free radical. Once formed, it reacts with ClO• to form BrCl and O_2. BrCl, in turn, reacts with sunlight to break into Cl• and Br•, both of which react with O_3 and form O_2.

a. Represent this information with a set of equations similar to those shown for the Chapman cycle.
b. What is the net equation for this cycle?

Answer:

a. $BrO\bullet + ClO\bullet \rightarrow BrCl + O_2$
$BrCl + \text{sunlight} \rightarrow Br\bullet + Cl\bullet$
$Br\bullet + O_3 \rightarrow BrO\bullet + O_2$
$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$
b. Net reaction: $2O_3 \rightarrow 3O_2$

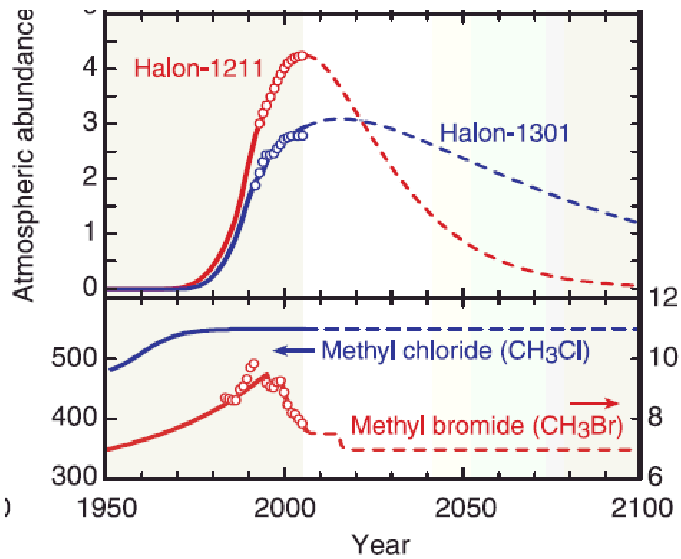
48. Polar stratospheric clouds (PSCs) play an important role in stratospheric ozone depletion.

a. Why do PSCs form more often in Antarctica than in the Arctic?
b. Reactions occur more quickly on the surface of PSCs than in the atmosphere. One such reaction is the reaction of hydrogen chloride and chlorine nitrate ($ClONO_2$), two species that do not deplete ozone, to produce a chlorine molecule and nitric acid (HNO_3). Write the chemical equation.
c. The chlorine molecule produced does not deplete ozone either. However, when the Sun returns to the Antarctic in the springtime, it is converted to a species that does. Show how with a chemical equation.

Answer:

a. See Figure 2.17. Most months, the Arctic is not cold enough for PSCs to form.
b. $HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$
The nitric acid remains bound to the ice, but the chlorine gas is released to the atmosphere.
c. In the atmosphere and in the presence of sunlight, $Cl_2 \rightarrow 2Cl\bullet$

49. Consider this graph that shows the atmospheric abundance of bromine-containing gases from 1950 to 2100.



Source: UNEP, "Twenty Questions and Answers about the Ozone Layer – 2006 update", page 35.

a. Halon-1301 is $CBrF_3$ and Halon-1211 is $CClBrF_2$. Why were these compounds once manufactured?

b. Compare the patterns for Halon-1211 and Halon-1301. Why doesn't Halon-1301 drop off as quickly?

c. In 2005, methyl bromide was phased out in the United States except for critical uses. Why is its future abundance predicted as a straight line, rather than tailing off?

Answer:

a. These compounds once were manufactured as fire suppressants. They are not water-based, so are excellent for specialized uses such as libraries, aircraft, and electronics. However, their production has been halted because they have high ozone depleting potentials (ODPs).

b. The two halons have different atmospheric lifetimes. According to data from the U.S. EPA, http://www.epa.gov/Ozone/science/ods/classone.html (accessed February 2010), the values are 65 years and 16 years, respectively, for Halon-1301 and Halon-1211. A more interesting question is why the different lifetimes, which is beyond the scope of this text.

c. At the time this graph was drawn, it was thought that no substitutes would be found for some uses of methyl bromide. However, it now is looking more likely that substitutes will be found.

Exploring Extensions

50. Chapter 1 discussed the role of nitrogen monoxide (NO) in forming photochemical smog. What role, if any, does NO play in stratospheric ozone depletion? Are NO sources the same in the stratosphere as in the troposphere?

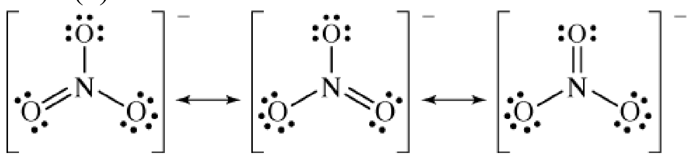
Answer:

NO in the stratosphere can act as a catalyst for the destruction of ozone. Although most of the NO in the stratosphere comes from natural origins, additional NO could be contributed directly to the stratosphere by supersonic transport (SST) planes. Before their grounding, the Anglo-French Concorde was the only commercial plane flying at such high altitudes.

51. Resonance structures can be used to explain the bonding in charged groups of atoms as well as in neutral molecules, such as ozone. The nitrate ion, NO_3^-, has one additional electron plus the outer electrons contributed by nitrogen and oxygen atoms. That extra electron gives the ion its charge. Draw the resonance structures, verifying that each obeys the octet rule.

Answer:

5 + 3(6) + 1 = 24 electrons



52. Although oxygen exists as O_2 and O_3, nitrogen exists only as N_2. Propose an explanation for these facts. *Hint:* Try drawing a Lewis structure for N_3.

Answer:

O_2, O_3, and N_2 all have an even number of valence electrons. In contrast, N_3 has 15 valence electrons. Molecules with odd numbers of electrons cannot follow the octet rule and are more reactive.

53. The chemical formulas for a CFC, such as CFC-11 (CCl_3F), can be figured out from its code number by adding 90 to it to get a three-digit number. For example, with CFC-11 you get 90 + 11 = 101. The first digit is the # of C atoms, the second is the # of H atoms, and the third is the # of F atoms. Accordingly, CCl_3F has 1 C atom, no H atoms, and 1 F atom. All remaining bonds are assumed to be chlorine.

a. What is the chemical formula for CFC-12?

b. What is the code number for CCl_4?

c. Does this "90" method work for HCFCs? Use HCFC-22 ($CHClF_2$) in explaining your answer.

d. Does this method work for halons? Use Halon-1301 (CF_3Br) in explaining your answer.

Answer:

a. 90 + 12 = 102. The compound contains one carbon atom, no hydrogen atoms, and two fluorine atoms. The chemical formula for CFC-12 is CCl_2F_2.

b. CCl_4 contains 1 carbon atom, 0 hydrogen atoms, and 0 fluorine atoms. Therefore, the code number for CCl_4 is 100 or 90 + 10. The name is CFC-10.

c. Yes the "90" method will work for HCFCs. 90 + 22 = 112, so HCFC-22 would be composed of 1 carbon atom, 1 hydrogen atom, and 2 fluorine atoms and its chemical formula would be CHF_2Cl.

d. No this method will not work for halons as there is no guideline for handling bromine.

54. Many different types of ozone generators ("ozonators") are on the market for sanitizing air, water, and even food. They are often sold with a slogan such as this one from a pool store. "Ozone, the world's most powerful sanitizer!"

a. What claims are made for ozonators intended to purify air?

b. What risks are associated with these devices?

Answer:

a. Ozonators typically produce ozone either from an electrical discharge or with UV light. The former is similar to what occurs in a thunderstorm when lightning splits O_2 molecules to form O atoms. The latter uses UV-C light to split O_2 molecules. In either case, the O atoms then react with another oxygen molecule to produce ozone. The ozone produced works as an effective disinfectant. It can react with many biological molecules, thereby being effective against undesired microbes and viruses. It also can react with many molecules that produce odors.

b. Search the web for examples. Claims include that ozonators can:

- destroy odors; tobacco, smoke, pet, cooking, and chemical
- kill bacteria and airborne viruses
- remove allergy causing pollen and microbes
- prevent mold and mildew, the leading cause of Legionnaires Disease
- eliminate toxic fumes from printing, plating processes, hair and nail salons

c. Again search the web for examples. Claims include that ozonators can:

- purify water in holding tanks and emergency storage water tanks
- purify drinking water from well sources or city water supplies
- remove undesirable tastes, odors, and colors.

d. Ozonators are used to sterilize materials and tools used in medical procedures. Unlike large commercial applications such as those to purify air or water, medical ozonators are small enough to be portable and can store the sterilized implements until ready for use. Ozonators work well in sterilizing synthetic sutures used for wound closure.

55. The effect a chemical substance has on the ozone layer is measured by a value called its *ozone-depleting potential,* ODP. This is a numerical scale that estimates the lifetime potential stratospheric ozone that could be destroyed by a given mass of the substance. All values are relative to CFC-11, which has an ODP defined as equal to 1.0. Use those facts to answer these questions.

a. Name two factors that affect the ODP value of a compound and explain the reason for each one.

b. Most CFCs have ODP values ranging from 0.6 to 1.0. What range do you expect for HCFCs? Explain your reasoning.

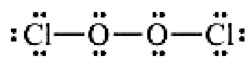
c. What ODP values do you expect for HFCs? Explain your reasoning.

Answer:

a. Factors include (1) the reactivity of the compound, because this in turn affects the length of time it will remains in the atmosphere, and (2) the presence of Cl or Br in the compound, because $Cl\bullet$ and $Br\bullet$, formed in the stratosphere from chlorine- and bromine- containing compounds, deplete ozone.

b. Most HCFCs, developed as replacements for CFCs, would be expected to have ODP values lower than those of the CFCs. HCFCs tend to be somewhat more reactive in the troposphere and thus do not accumulate in the stratosphere. Their ODP values range from 0.01 to 0.11.
c. HFCs were also developed as CFC substitutes. Without chlorine or bromine present, they generally do not have the potential to deplete stratospheric ozone. Their ODP values are 0.0.

56. Recent experimental evidence indicates that ClO• initially reacts to form Cl_2O_2.
a. Predict a reasonable Lewis structure for this molecule. Assume the order of atom linkage is Cl–O–O–Cl.
b. What effect does this evidence have on understanding the mechanism for the catalytic destruction of ozone by ClO•?

Answer:
a. Here is a possible Lewis structure. 

b. If Cl_2O_2 is the actual molecule, then it will have to be broken down by UV photons to ClO• free radicals before it can react with oxygen atoms as shown in equations 2.12a and 2.12b. This would add one additional decomposition reaction in the catalytic destruction of ozone.