The Islamic University of Gaza- Environmental Engineering Department
Environmental Chemistry I (EENV 2301)

CHAPTER 6: THE ATMOSPHERE AND ATMOSPHERIC CHEMISTRY

The Atmosphere and Atmospheric Chemistry
Physical Characteristics of the Atmosphere
Chemical and Photochemical Reactions in the Atmosphere
Acid–Base Reactions in the Atmosphere
Reactions of Atmospheric Oxygen and Nitrogen

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The atmosphere composes the thin layer of mixed gases covering Earth's surface.

Exclusive of water, atmospheric air is :

78.1% (by volume) nitrogen, 21.0% oxygen, 0.9% argon, and 0.03% carbon dioxide.

Normally, air is 1–3% water vapor by volume.

In addition, air contains a large variety of trace level gases at levels below 0.002%, including neon, helium, methane, krypton, nitrous oxide, hydrogen, xenon, sulfur dioxide, ozone, nitrogen dioxide, ammonia, and carbon monoxide.

The atmosphere is divided into several layers on the basis of temperature:

The troposphere, extending in altitude from the earth's surface to approximately **11 km**

The stratosphere, from about **11 km to approximately 50 km**.

The temperature of the troposphere ranges from an average of 15˚C at sea level to an average of -56˚C at its upper boundary.

The average temperature of the stratosphere increases from -56˚C at its boundary with the troposphere to –2˚C at its upper boundary.

The reason for this increase is absorption of solar ultraviolet energy by ozone (O_3) in the stratosphere.

photochemical reactions resulting from the absorption by molecules of light photons, designated hƱ.

The energy, E, of a photon of visible or ultraviolet light is given by the equation

E = hƱ, where

h is Planck's constant and

Ʊ is the frequency of light, which is inversely proportional to its wavelength.

Ultraviolet radiation has a higher frequency than visible light and is, therefore, more energetic and more likely to break chemical bonds in molecules that absorb it.

One of the most significant photochemical reactions is the one responsible for the presence of ozone in the stratosphere, which is initiated when O_2 absorbs highly energetic ultraviolet radiation in the stratosphere to form oxygen atoms, which react further to produce ozone, O_3.

Gaseous Oxides in the Atmosphere

Oxides of carbon, sulfur, and nitrogen are important constituents of the atmosphere and are pollutants at higher levels.

Of these, carbon dioxide, CO_2, is the most abundant.

It is a natural atmospheric constituent, and it is required for plant growth.

However, the level of **CO_2** in the atmosphere, now at about 365 parts per million (ppm) by volume, is increasing by about 1 ppm per year, which may well cause general atmospheric warming, the "greenhouse effect," with potentially very serious consequences for the global atmosphere and for life on earth.

Hydrocarbons and Photochemical Smog

The most abundant **hydrocarbon** in the atmosphere is **methane, CH_4**, released from underground sources as natural gas and produced by the fermentation of organic matter.

Methane is one of the least reactive atmospheric hydrocarbons and is produced by diffuse sources, so that its participation in the formation of pollutant photochemical reaction products is minimal.

The most significant atmospheric pollutant hydrocarbons are the reactive ones produced as automobile exhaust emissions.

Particulate Matter

Particles ranging from aggregates of a few molecules to pieces of dust readily visible to the naked eye are commonly found in the atmosphere .

Colloidal-sized particles in the atmosphere are called aerosols.

Some atmospheric particles, such as sea salt formed by the evaporation of water from droplets of sea spray, are natural and even beneficial atmospheric constituents.

Very small particles called condensation nuclei serve as bodies for atmospheric water vapor to condense upon and are essential for the formation of rain drops.

IMPORTANCE OF THE ATMOSPHERE

The atmosphere is a protective blanket that nurtures يغذي life on the Earth and protects it from the hostile معاد environment of outer space.

The atmosphere is the source of CO_2 for plant photosynthesis and of O_2 for respiration.

It provides the nitrogen that nitrogen-fixing bacteria and ammonia-manufacturing plants use to produce chemically bound nitrogen, an essential component of life molecules.

As a basic part of the hydrologic cycle the atmosphere transports water from the oceans to land, thus acting as the condenser in a vast solar-powered still.

In its essential role as a protective shield, the atmosphere absorbs most of the cosmic rays الأشعة الكونية from outer space and protects organisms from their effects.

It also absorbs most of the electromagnetic radiation from the sun, allowing transmission of significant amounts of radiation only in the regions of 300 –2500 nm (near-ultraviolet, visible, and near-infrared radiation) and 0.01– 40 m (radio waves).

By absorbing electromagnetic radiation below 300 nm, the atmosphere filters out damaging ultraviolet radiation that would otherwise be very harmful to living organisms.

Furthermore, because it reabsorbs much of the infrared radiation by which absorbed solar energy is re-emitted to space, the atmosphere stabilizes the earth's temperature, preventing the tremendous temperature extremes that occur on planets and moons lacking substantial atmospheres.

PHYSICAL CHARACTERISTICS OF THE ATMOSPHERE

Variation of Pressure and Density with Altitude

The density of the atmosphere decreases sharply with increasing altitude as a consequence of the gas laws and gravity.

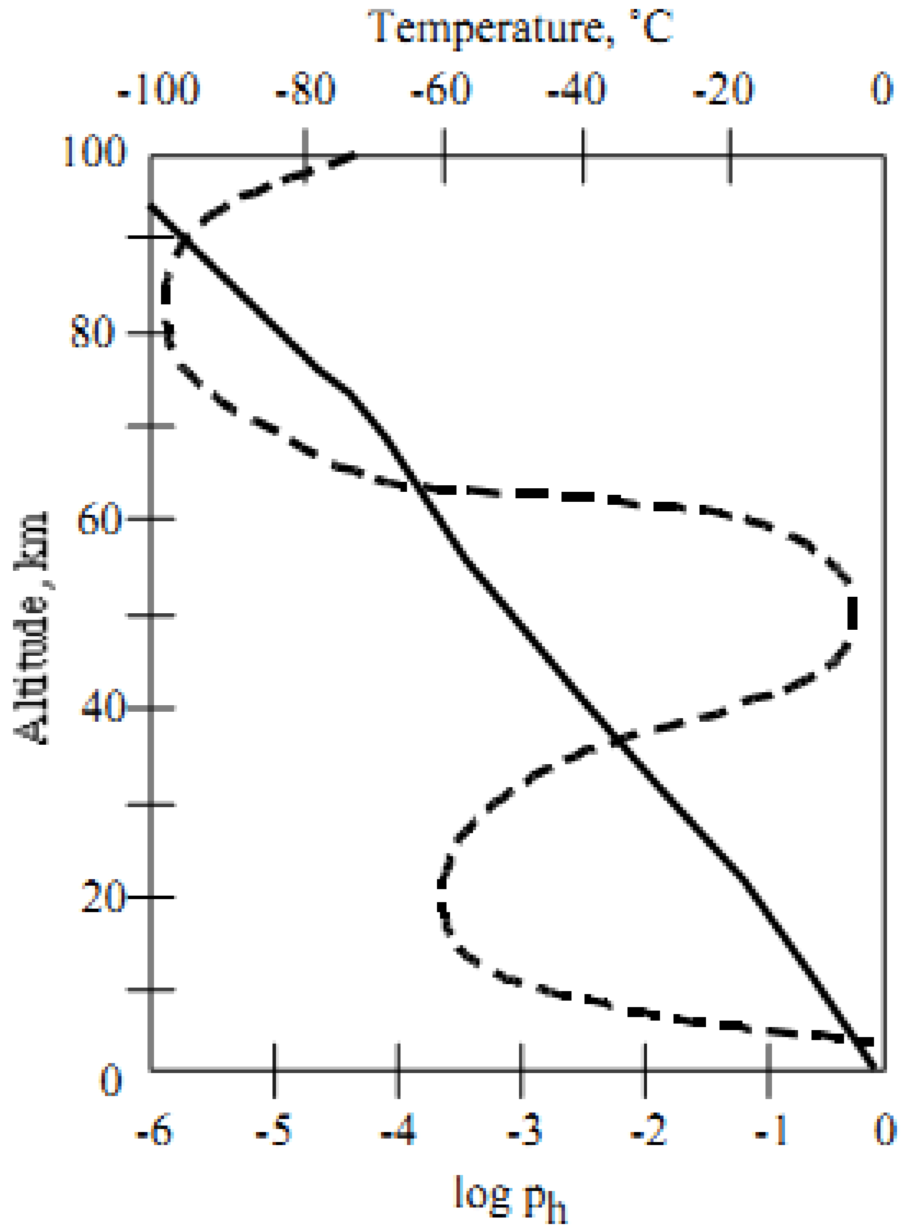
More than 99% of the total mass of the atmosphere is found within approximately 30 km of the earth's surface.

Although the total mass of the global atmosphere is huge, approximately 5.14 x 10^{15} metric tons, it is still only about one millionth of the earth's total mass.

The fact that atmospheric pressure decreases as an approximately exponential function of altitude largely determines the characteristics of the atmosphere.

The characteristics of the atmosphere vary widely with altitude, time (season), location (latitude), and even solar activity.

At very high altitudes, normally reactive species such as atomic oxygen, O, persist for long periods of time. That occurs because the pressure is very low at these altitudes such that the distance traveled by a reactive species before it collides with a potential reactant- its mean free path-is quite high. A particle with a mean free path of 1 x 10^{-6} cm at sea level has a mean free path greater than 1 x 10^{6} cm at an altitude of 500 km, where the pressure is lower by many orders of magnitude.



Variation of pressure (solid line) and temperature (dashed line) with altitude.

Stratification of the Atmosphere

The atmosphere is **stratified on the basis of the temperature/density relationships** resulting from interactions between physical and photochemical (light-induced chemical phenomena) processes in air.

The lowest layer of the atmosphere extending from sea level to an altitude of 10-16 km is the **troposphere**, characterized by a generally homogeneous composition of major gases other than water and decreasing temperature with increasing altitude from the heat-radiating surface of the earth.

The upper limit of the troposphere, which has a temperature minimum of about -56˚C, varies in altitude by a kilometer or more with atmospheric temperature, underlying terrestrial surface, and time.

The homogeneous composition of the troposphere results from constant mixing by circulating air masses.

However, the water vapor content of the troposphere is extremely variable because of cloud formation, precipitation, and evaporation of water from terrestrial water bodies.

The very cold temperature of the tropopause layer at the top of the troposphere serves as a barrier that causes water vapor to condense to ice so that it cannot reach altitudes at which it would photodissociate through the action of intense high-energy ultraviolet radiation.

If this happened, the hydrogen produced would escape the earth's atmosphere and be lost. (Much of the hydrogen and helium gases originally present in the earth's atmosphere were lost by this process.)

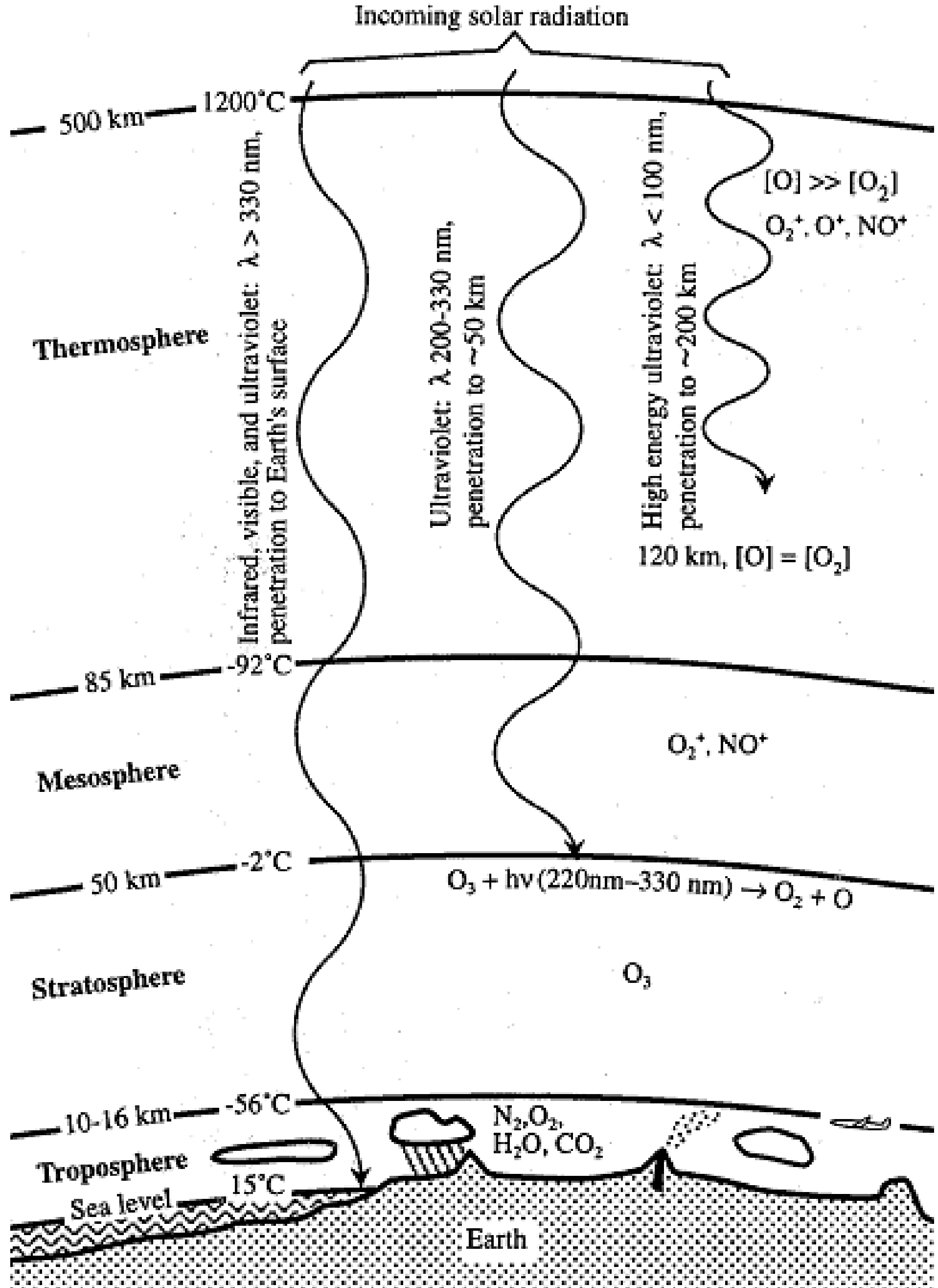
The atmospheric layer directly above the troposphere is the **stratosphere**, in which the temperature rises to a maximum of about -2˚C with increasing altitude.

This phenomenon is due to the presence of ozone, O_3, which can reach a level of around 10 ppm by volume in the mid-range of the stratosphere.

The absence of high levels of radiation-absorbing species in the **mesosphere** immediately above the stratosphere results in a further temperature decrease to about -92˚C at an altitude around 85 km.

The upper regions of the mesosphere and higher define a region, called the **exosphere**, from which molecules and ions can completely escape the atmosphere.

Extending to the far outer reaches of the atmosphere is the **thermosphere**, in which the highly rarified gas الغاز المخلخل reaches temperatures as high as1200˚C by the absorption of very energetic radiation of wavelengths less than approximately 200 nm by gas species in this region.



Incoming solar radiation
500 km
1200°C
Infrared, visible, and ultraviolet: λ > 330 nm, penetration to Earth's surface
Ultraviolet: λ 200-330 nm, penetration to ~50 km
High energy ultraviolet: λ < 100 nm, penetration to ~200 km
[O] >> [O2]
O2+, O+, NO+
Thermosphere
120 km, [O] = [O2]
85 km
-92°C
O2+, NO+
Mesosphere
50 km
-2°C
O3 + hν (220nm–330 nm) → O2 + O
Stratosphere
O3
10-16 km
-56°C
N2,O2,
H2O, CO2
Troposphere
15°C
Sea level
Earth

Photochemical Processes

The absorption by chemical species of light, broadly defined here to include ultraviolet radiation from the sun, can bring about reactions, called photochemical reactions.

Photochemical reactions, which are induced by intense solar radiation, play a very important role in determining the nature and ultimate fate of a chemical species in the atmosphere.

Nitrogen dioxide, NO_2, is one of the most photochemically active species found in a polluted atmosphere and is an essential participant in the smog-formation process.

A species such as NO_2 may absorb light of energy h℧, producing an electronically excited molecule,

$$NO_2 + h\mho \longrightarrow NO_2^*$$

Electronically excited molecules are one of the three relatively reactive and unstable species that are encountered in the atmosphere and are strongly involved with atmospheric chemical processes.

The other two species are atoms or molecular fragments with unshared electrons, called free radicals, and ions consisting of electrically charged atoms or molecular fragments.

The reactions that occur following absorption of a photon of electromagnetic radiation to produce an electronically excited species are largely determined by the way in which the excited species loses its excess energy. This can occur by one of the following processes:

Physical quenching: Loss of energy to another molecule or atom (M),followed by dissipation of the energy as heat

$$O_2^* + M \longrightarrow O_2 + M \quad \text{(higher translational energy)}$$

Dissociation of the excited molecule (the process responsible for the predominance of atomic oxygen in the upper atmosphere)

$$O_2^* \longrightarrow O + O$$

Direct reaction with another species $O_2^* + O_3 \longrightarrow 2O_2 + O$

Luminescence consisting of loss of energy by the emission of electromagnetic radiation

$$NO_2^* \longrightarrow NO_2 + h\upsilon$$

If the re-emission of light is almost instantaneous, luminescence is called **fluorescence**, and if it is significantly delayed, the phenomenon is **phosphorescence**. **Chemiluminescence** is said to occur when the excited species (such as NO_2^* below) is formed by a chemical process:

$$O_3 + NO \longrightarrow NO_2^* + O_2 \text{ (higher energy)}$$

Intermolecular energy transfer in which an excited species transfers energy to another species that then becomes excited

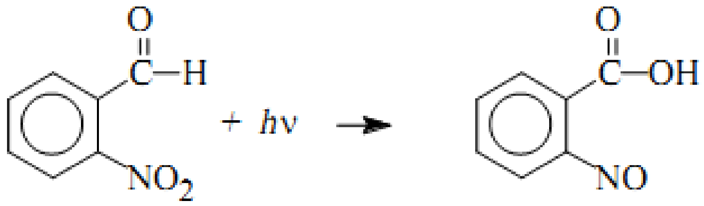
$$O_2^* + Na \longrightarrow O_2 + Na^*$$

A subsequent reaction by the second species is called a **photosensitized** reaction.

Intramolecular transfer in which energy is transferred within a molecule

$XY^* \longrightarrow XY^\dagger$ (where † denotes another excited state of the same molecule)

Spontaneous isomerization as in the conversion of o-nitrobenzaldehyde to o-nitrosobenzoic acid, a reaction used in chemical actinometers to measure exposure to electromagnetic radiation:



Photoionization through loss of an electron

$$N_2^* \longrightarrow N_2^+ + e^-$$

Chemical and Biochemical Processes in Evolution تطور of the Atmosphere

It is now widely believed that the earth's atmosphere originally was very different from its present state and that the changes were brought about by biological activity and accompanying chemical changes.

Approximately 3.5 billion years ago, when the first primitive بدائي life molecules were formed, the atmosphere was probably free of oxygen and consisted of a variety of gases such as CO_2, water vapor, and perhaps even CH_4, NH_3, and H_2.

The atmosphere was bombarded by intense, bond-breaking ultraviolet light which, along with lightning and radiation from radionuclides, provided the energy to bring about chemical reactions that resulted in the production of relatively complicated molecules, including even amino acids and sugars, which are produced and used by living organisms.

From the rich chemical mixture in the sea, life molecules evolved. Initially, these very primitive life forms derived their energy from fermentation of organic matter formed by chemical and photochemical processes, but eventually they gained the capability to produce organic matter, "$\{CH_2O\}$," by photosynthesis:

$$CO_2 + H_2O + h\nu \longrightarrow \{CH_2O\} + O_{2\,(g)}$$

Photosynthesis released oxygen, thereby setting the stage for the massive biochemical transformation that resulted in the production of almost all the atmosphere's O .

The elemental oxygen initially produced by photosynthesis was probably quite toxic to primitive life forms.

However, much of this oxygen was converted to iron oxides by reaction with soluble iron(II):

$$4Fe_2^{+} + O_2 + 4H_2O \longrightarrow 2Fe_2O_3 + 8H^{+}$$

The existence of enormous deposits of iron oxides provides major evidence for the liberation of free O_2 in the primitive atmosphere.

ACID-BASE REACTIONS IN THE ATMOSPHERE

Acid-base reactions occur between acidic and basic species in the atmosphere.

The atmosphere is normally at least slightly acidic because of the presence of a low level of carbon dioxide, which dissolves in atmospheric water droplets and dissociates slightly:

$$CO_{2\,(g)} \xrightarrow{\text{Water}} CO_{2\,(aq)}$$

$$CO_{2\,(aq)} + H_2O \longrightarrow H^+ + HCO_3^-$$

Atmospheric sulfur dioxide forms a somewhat stronger acid when it dissolves in water:

$$SO_{2\,(g)} + H_2O \longrightarrow H^+ + HSO_3^-$$

In terms of pollution, however, strongly acidic HNO_3 and H_2SO_4 formed by the atmospheric oxidation of N oxides, SO_2, and H_2S are much more important because they lead to the formation of damaging acid rain.

As reflected by the generally acidic pH of rainwater, basic species are relatively less common in the atmosphere.

Particulate calcium oxide, hydroxide, and carbonate can get into the atmosphere from ash and ground rock, and can react with acids such as in the following reaction:

$$Ca(OH)_{2\,(s)} + H_2SO_{4\,(aq)} \longrightarrow CaSO_{4\,(s)} + 2H_2O$$

The most important basic species in the atmosphere is gas-phase ammonia, NH_3.

The major source of atmospheric ammonia is from biodegradation of nitrogen-containing biological matter and from bacterial reduction of nitrate:

$$NO_3^-{}_{(aq)} + 2\{CH_2O\}(\text{biomass}) + H^+ \longrightarrow NH_{3\,(g)} + 2CO_2 + H_2O$$

Ammonia is particularly important as a base in the air because it is the only water-soluble base present at significant levels in the atmosphere.

When it is dissolved in atmospheric water droplets, ammonia plays a strong role in neutralizing atmospheric acids, as shown by the following reactions:

$$NH_{3\,(aq)} + HNO_{3(aq)} \longrightarrow NH_4NO_{3\,(aq)}$$

$$NH_{3\,(aq)} + H_2SO_{4(aq)} \longrightarrow NH_4HSO_{4\,(aq)}$$

These reactions have three effects:

(1) They result in the presence of NH_4^+ ion in the atmosphere as dissolved or solid salts,

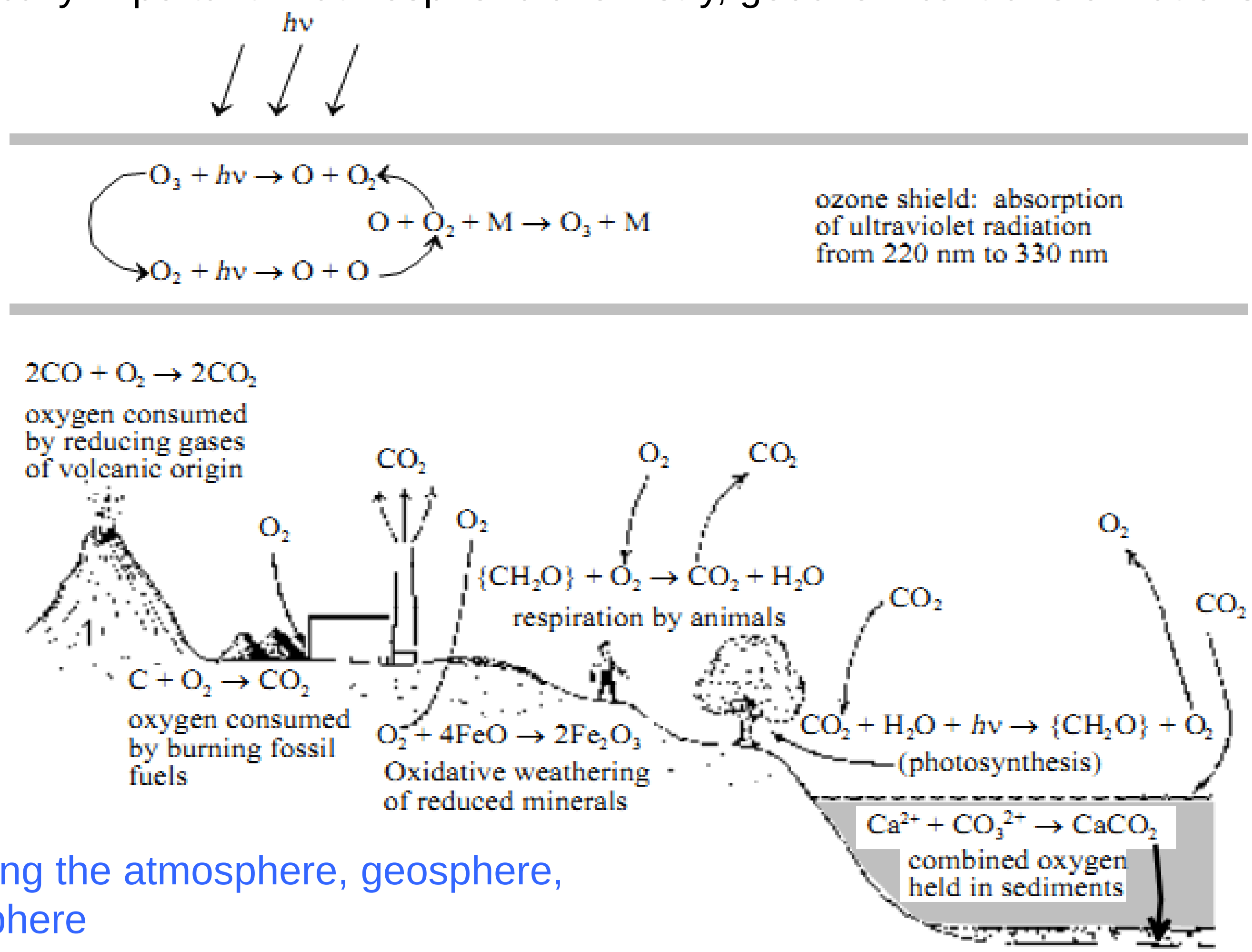
(2) they serve in part to neutralize acidic consituents of the atmosphere, and

(3) they produce relatively corrosive ammonium salts.

REACTIONS OF ATMOSPHERIC OXYGEN

Some of the primary features of the exchange of oxygen among the atmosphere, geosphere, hydrosphere, and biosphere are summarized in Figure below.

The oxygen cycle is critically important in atmospheric chemistry, geochemical transformations, and life processes.



Oxygen exchange among the atmosphere, geosphere, hydrosphere, and biosphere

Oxygen in the troposphere plays a strong role in processes that occur on the earth's surface.

Atmospheric oxygen takes part in energy-producing reactions, such as the burning of fossil fuels: **CH_4(in natural gas) + $2O_2$ $\longrightarrow$ CO_2 + $2H_2O$**

Atmospheric oxygen is utilized by aerobic organisms in the degradation of organic material.

Some oxidative weathering processes consume oxygen, such as
$4FeO + O_2 \longrightarrow 2Fe_2O_3$

Oxygen is returned to the atmosphere through plant photosynthesis:
CO_2 + H_2O + hʊ $\longrightarrow$ {CH_2O} + O_2

Atomic oxygen is produced by a photochemical reaction: **O_2 + hʊ $\longrightarrow$ O + O**.

The oxygen-oxygen bond is strong (120 kcal/mole) and ultraviolet radiation in the wavelength regions 135–176 nm and 240–260 nm is most effective in causing dissociation of molecular oxygen.

Oxygen atoms in the atmosphere can exist in the ground state (O) and in excited states (O*). These are produced by the photolysis of ozone, which has a relatively weak bond energy of 26 kcal/mole at wavelengths below 308 nm,
O_3 + hʊ ($\lambda < 308$ nm) $\longrightarrow$ O* + O_2 or by highly energetic chemical reactions such as :**O + O + O $\longrightarrow$ O_2 + O***

Ozone, O_3, has an essential protective function because it absorbs harmful ultraviolet radiation in the stratosphere and serves as a radiation shield, protecting living beings on the earth from the effects of excessive amounts of such radiation.

It is produced by a photochemical reaction,

$$O_2 + h\upsilon \longrightarrow O + O$$

(where the wavelength of the exciting radiation must be less than 242.4 nm), followed by a three-body reaction,

$$O + O_2 + M \longrightarrow O_3 + M$$

(increased energy) in which M is another species, such as a molecule of N_2 or O_2, which absorbs the excess energy given off by the reaction and enables the ozone molecule to stay together.

The region of maximum ozone concentration is found within the range of 25–30 km high in the stratosphere where it may reach 10 ppm.

Ozone absorbs ultraviolet light very strongly in the region 220–330 nm. If this light were not absorbed by ozone, severe damage would result to exposed forms of life on the earth.

Absorption of electromagnetic radiation by ozone converts the radiation's energy to heat and is responsible for the temperature maximum encountered at the boundary between the stratosphere and the mesosphere at an altitude of approximately 50 km.

The reason that the temperature maximum occurs at a higher altitude than that of the maximum ozone concentration arises from the fact that ozone is such an effective absorber of ultraviolet light.

Therefore, most of the ultraviolet radiation absorbed by ozone is absorbed in the upper stratosphere, where it generates heat, and only a small fraction reaches the lower altitudes, which remain relatively cool.

REACTIONS OF ATMOSPHERIC NITROGEN

The 78% by volume of nitrogen contained in the atmosphere constitutes an inexhaustible reservoir of that essential element.

A significant amount of nitrogen is fixed in the atmosphere by lightning, which provides the high energy needed to dissociate stable molecules of N_2.

Some nitrogen is also fixed by combustion processes, particularly in internal combustion and turbine engines.

Before the use of synthetic fertilizers reached its current high levels, chemists were concerned that denitrification processes in the soil would lead to nitrogen depletion on the Earth.

Now, with millions of tons of synthetically fixed nitrogen being added to the soil each year, major concern has shifted to possible excess accumulation of nitrogen in soil, fresh water, and the oceans.

Unlike oxygen, which is almost completely dissociated to the monatomic form in higher regions of the thermosphere, molecular nitrogen is not readily dissociated by ultraviolet radiation.

However, at altitudes exceeding approximately 100 km, atomic nitrogen is produced by photochemical reactions:

$$N_2 + h\nu \longrightarrow N + N$$

Pollutant oxides of nitrogen, particularly NO_2, are key species involved in air pollution and the formation of photochemical smog.

For example, NO_2 is readily dissociated photochemically to NO and reactive atomic oxygen:

$$\mathbf{NO_2 + h\upsilon \longrightarrow NO + O.}$$

This reaction is the most important primary photochemical process involved in smog formation.