CHEM 351: ENVIRONMENTAL CHEMISTRY

INTRODUCTION

Environmental Chemistry deals with the origins, transport, reactions, effects and fates of chemical species in the water, air, terrestrial and living environments. It overlaps with different branches of chemistry such as organic chemistry, analytical chemistry, physical chemistry, photochemistry, geochemistry and biological chemistry and also includes many widely different fields such as physics, life sciences, agricultural sciences, medical sciences, public health and sanitary engineering.

Environmental Segments:

The environment consists of various segments such as atmosphere, hydrosphere, lithosphere and biosphere.

Atmosphere

The atmosphere is the protective blanket of gases, which is surrounding the earth. It protects the earth from the hostile environment of outer space.

Significance of the Atmosphere

The atmosphere protects life on earth by serving the following functions:

- Absorbs the energetic ultraviolet radiation emitted by the sun (tissue damaging UV radiation below 300 nm) while allowing the passing of important visible radiations only in the regions of 300 – 2500 nm (near UV, Visible, and near IR) and 0.01 – 40 meters (radio waves). It also absorbs IR (Infrared) radiations reemitted from the earth and thus controls the temperature of the earth through heat retention, making possible a comfortable mean temperature of ±15°C.

- Prevents excessive heating of surface of the earth at day and excessive cooling at night thereby reducing the temperature variations.
- Contains nitrogen, oxygen and carbon dioxide gases essential for plant growth and for respiration.
- It protects the surface of the earth and all life existing on earth from small meteorites that heat up in the atmosphere due to friction.
- Serves an integral part in the bio-geo chemical cycles of C, N, O, P and S.
- Helps in flow of energy and water vapours through dynamic processes of air flow thus the atmosphere transports water from ocean to land.
- Helps in radio communication.
- Helps in movement of aircrafts.
- Aids in dissipation, dispersion and decomposition of pollutants.

Hydrosphere:

Water, in its three phases, liquid water, ice and water vapour, is highly abundant at the Earth's surface, having a volume of 1.4 billion km^3. Nearly all of this water (>97%) is stored in the oceans, while most of the rest forms the polar ice-caps and glaciers. Continental freshwaters represent less than 1% of the total volume, and most of this is groundwater. The atmosphere contains comparatively little water (as vapour). Collectively, these reservoirs of water are called the hydrosphere.

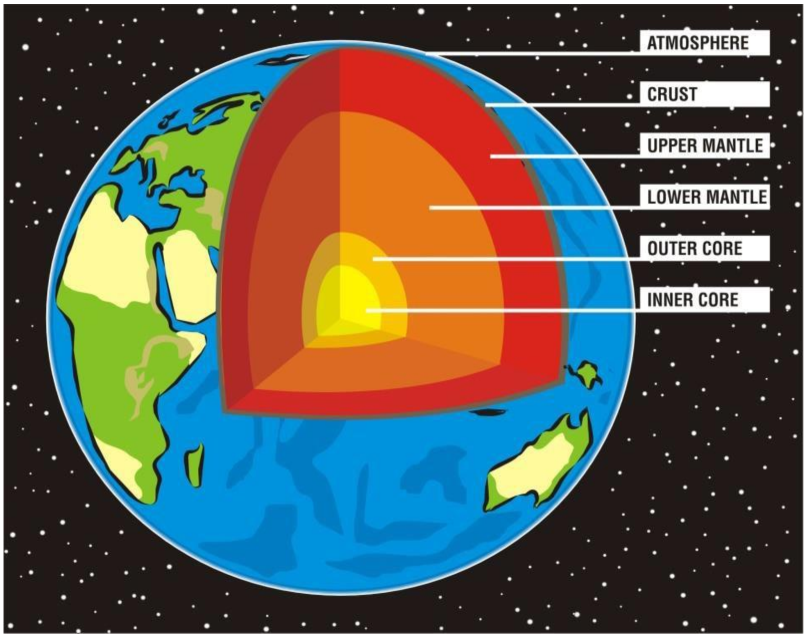
The distribution of earth's water supply is shown in the fig below:

The extent of the use of available fresh water for various purposes is dependent on the locality.

The major problem with global water supply is it's non-uniform distribution, since people in areas with low precipitation often consume more than people in regions with more rainfall.

Lithosphere

- The earth is divided into layers as shown in the figure below:



- The lithosphere consists of the upper mantle and the crust.

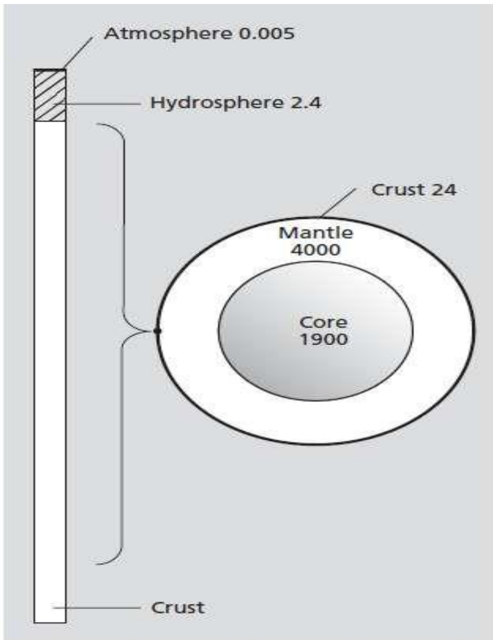
- The crust is the earth's outer skin that is accessible to human. The crust consists of rocks and soil of which the latter is the important part of lithosphere.

Biosphere:

- The biosphere refers to the realm of living organisms and their interactions with the environment (VIZ: atmosphere, hydrosphere and lithosphere)
- The biosphere is very large and complex and is divided into smaller units called ecosystems.
- Plants, animals and microorganisms which live in a definite zone along with physical factors such as soil, water and air constitute an ecosystem.
- Within each ecosystem there are dynamic inter relationships between living forms and their physical environment.

STRUCTURE AND COMPOSITION OF THE ATMOSPHERE

The atmosphere is the smallest of the Earth's geological reservoirs.



Relative sizes of the major reservoirs of the Earth. Units, 10^{24} g.

It is this limited size that makes the atmosphere potentially so vulnerable to contamination. Even the addition of a small amount of material can lead to significant changes in the way the atmosphere behaves. The contaminants in the atmosphere disperses rapidly unlike the spread of contaminants in the ocean which is much slower while in the other reservoirs of the Earth it takes place only over geological timescales of millions of years.

It is the thick blanket of air which envelopes our planet and helps sustain life. The atmospheric gases which are used in respiration and photosynthesis are called 'air'. The atmosphere of earth contains mixture of gases which are forced to be maintained near the earth's surface by gravity. An increase in altitude will decrease the density of atmosphere.

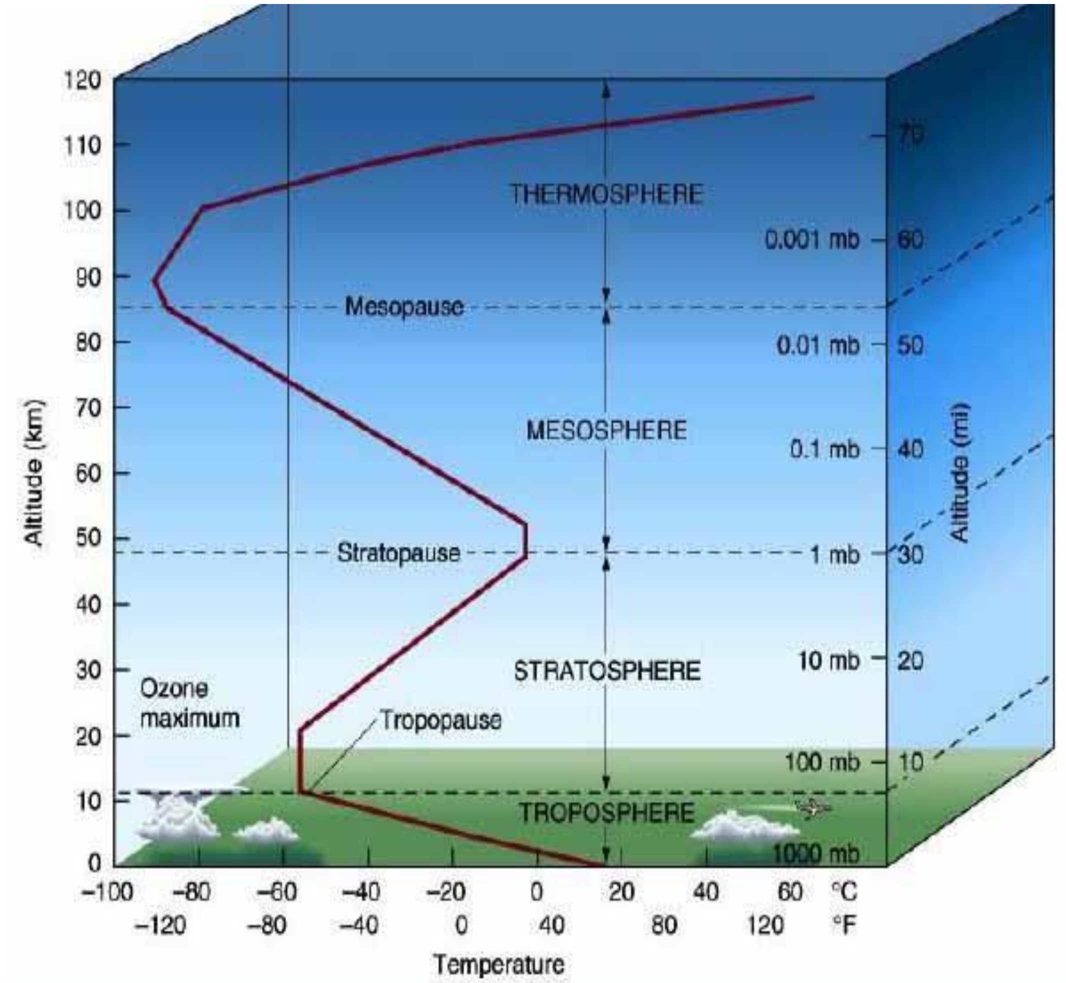
Maximum atmosphere is located close to the surface, within 16 kilometres. Though the atmosphere extends into outer space and there is no distinct border between them, but an imaginary line called the Kármán Line which is approximately at the height of 100 km is called as the boundary of Earth's atmosphere.

Composition of the Atmosphere

Bulk composition of the atmosphere is quite similar all over the Earth because of the high degree of mixing within the atmosphere. This mixing is driven in a horizontal sense by the rotation of the Earth. Vertical mixing is largely the product of heating of the surface of the Earth by incoming solar radiation. However, some parts of the atmosphere are not so well mixed and here quite profound changes in bulk composition are found.

The atmosphere is having 78.08% nitrogen (N_2), 20.95% oxygen (O_2) and about 1% other gases.

Structure of the Atmosphere



The Earth's atmosphere consists of a few zones or layers like spherical shells. The layered structure of the atmosphere has been classified on two major considerations: Thermal characteristics, Chemical characteristics.

- On the basis of the characteristics of temperature and air pressure the atmosphere is divided into five vertical zones i.e. Troposphere, Stratosphere, Mesosphere, Thermosphere, Exosphere.
- It is worth mentioning that majority of scientists have included Ozonosphere into Stratosphere and Ionosphere into Exosphere.

Troposphere

Troposphere is closest layer to the earth's surface. It is derived from the word 'Tropos' meaning turbulent. So, the layer in which we live is troposphere. It is about 18 km above the sea level at the equator and 7 km at poles.

75% of the atmospheric gases are present in this layer and almost all of the dust particles and water vapors. All weather phenomenon like cloud formation, winds, rainfall, snowfall takes place in this layer.

The air below this layer is warmer than any other layer because it is heated from the earth's surface below. The layer of air, which is warm, tends to rise up, and a pocket of cold air flows to cover the space, giving rise to wind movement.

The temperature will decrease at a rate of about 6.5 °C per km as the altitude increases. The average temperature near the surface is 15°C while it is -57° C at the top.

Pressure, moisture content and density of air also decrease with height thinning of air. That is why people experience breathlessness at high altitudes in mountains.

The troposphere ends when there is variation in temperature with height. The decrease of temperature stops at this point and hence it represents a cold point. This area, which is about 1.5 km thick, is the top of troposphere and bottom of stratosphere, is known as tropopause. The inversion of temperature beyond tropopause prevents further convection of air thereby confining most of the weather phenomenon in troposphere.

Stratosphere

Stratosphere is the second layer of earth's atmosphere. The term stratosphere is derived from a Greek word "strata" which means arrangement in horizontal layers. It starts at the top of tropopause and is 50 km above the sea level. This layer is characterized by near absence of weather phenomena because of stable condition, dry air and concentration of ozone gas.

Approximately 99% of the atmosphere is located up to this height, which includes almost all the gases. Weather balloons and jet aircrafts fly in this region, as the air present in this layer is very thin. This increases the fuel efficiency of the aircrafts.

The stratosphere also contains the ozone layer; at a height of about 30 km. This portion of stratosphere is known as ozonosphere. The ozone layer is thinnest near the equator and its thickness increases towards the pole, though there are seasonal fluctuations.

Ozone – which is a mainly formed from photochemical smog – is considered to be dangerous for health if it reaches the ground level or near the surface of the earth.

However, in the stratosphere, the high-energy UV radiation is absorbed by the ozone layer and heats up the stratosphere. This prevents skin cancer and damage to vegetation.

The ozone layer is created in the stratosphere when the oxygen molecules (O_2) absorb UV radiations (240 nm) and dissociate to give atomic oxygen (O) which immediately react with another O_2 molecule and results in the formation of an ozone (O_3) molecule:

$$O_2 \xrightarrow{UV} O + O$$

$$O + O_2 + M \xrightarrow{UV} O_3 + M$$

Although, the absorption of UV radiation in the stratosphere leads to dissociation of ozone molecules, the ozone layer density is maintained by the reformation of ozone:

$$O_3 \xrightarrow{UV} O + O_2$$

$$O + O_3 \rightarrow 2O_2$$

This process is called the Chapman cycle and M is a third body, which could be a random air molecule (O_2 or N_2).

Depletion of ozone would result in the rise of temperature of the ground surface and lower atmosphere. The main culprits of ozone destruction are halogenated gases called Chlorofluorocarbons, Halons (Alkanes linked halogens) and Nitrogen oxide.

As the height increases temperature in the stratosphere also increases, with the base temperature being close to −60 °C and close to freezing at the top. This is because of absorption of ultraviolet solar radiation by ozone, which may reach a level of around 10 ppm by volume in the mid-range of the stratosphere and lesser density of air. Since, the top layer is hottest and bottom is coldest, the temperature stratification takes place with little or no mixing of layers.

The stratification has a disadvantage too. Because there is no vertical convection in the stratosphere, dissipation and dispersion of materials, do not take place implying that Chlorofluorocarbons (CFCs) and aerosols from volcanic eruptions and meteorite impacts can stay in the stratosphere for prolonged periods of time resulting in damage to the ozone layer and alteration of global climate. The periods of existence of ozone hole have also seen a considerable increase in the reported incidents of skin cancer. The layer, which is top of the stratosphere and bottom of mesosphere (the next layer to stratosphere), is known as stratopause. Here, the temperature becomes constant with altitude until it again starts decreasing in the mesosphere.

Mesosphere

It is the middle layer of the earth's atmosphere. The name derives from the Greek word 'misos' meaning middle. This layer starts at 50 km above the sea level and extends to about 85 km. The air in this layer is very thin and molecules are at long distance from each other. Not much is known about this layer because weather balloons and jet aircrafts do not fly so high and it is too low an orbit for satellites and space shuttles. Some scientific studies have been made using sounding rockets that are not required to go into orbit. It is found that meteors generally burn up in the mesosphere. Thus, this layer protects the surface of earth from being pockmarked with craters.

The temperature of this layer also decreases with increase in altitude. The temperature of upper layer of mesosphere is even less than -100°C. This is due to the absence of high levels of radiation absorbing species, particularly ozone. The principal chemical species in this region are O_2^+ and NO.

This sphere ends at the mesopause. It marks the minimum temperature of mesosphere (making it the coldest part of earth also) and is the bottom of the next layer – the thermosphere – of the atmosphere.

Thermosphere

It is the fourth and widest among all layers of the atmosphere. It is at 90 km or starts from the top of mesopause to between 500 and 1,000 km, varying with solar activity. When more high energy radiations are emitted by the sun, the thermosphere expands under heat and thus, its height at top varies. The air is so thin in this layer, that it is generally considered to be part of outer space.

The Kármán Line, the boundary of the atmosphere also lies in this region. The layer also consists of many satellites and space shuttles orbit.

Temperature inversion takes place in thermosphere and temperature increases as one goes up. The temperatures can range from 500 °C to 2,000 °C or higher, depending upon the position and activity of the sun. However, the air feels cold because the molecules are so far apart that a molecule may travel up to 1 km before collision with another molecule.

Most of the X-rays and UV radiations emitted by the sun are absorbed in the thermosphere. In this layer dissociation of the molecules into atoms, ions and free electrons is done by high energy radiation. The ionization process increases with increase in sun's activity. The ions create an electrical layer, known as the ionosphere. The top of thermosphere is called thermopause. It is also called exobase, because it is the bottom of the exosphere.

Exosphere

This is the outermost layer of earth's atmosphere. It starts from the top of thermosphere and extends up to a height of 10,000 km into space. The atmosphere mainly consists of hydrogen and helium, which can escape into space. So, the air is so thin here that it is almost a vacuum. Thus, the atoms and molecules have to cover hundreds of kilometers before colliding with each other. Temperature of exosphere is very high because the particles are directly heated from solar radiation. However, it doesn't appear so high because there are too few particles and so there is not much transfer of energy because inter-molecular collisions are limited.

Trace constituents in the atmosphere

The atmosphere is in a steady state on a large scale. This implies that it has sources, a reservoir (i.e. the atmosphere itself) and removal processes, all in delicate balance. The sources need to be quite stable over the long term. If they are not, then the balance will shift. The best-known, and most worrying, example of such a shift is the increasing magnitude of the CO_2 source because of the consumption of vast amounts of fossil fuel by human activities. This has given rise to a continuing increase in the CO_2 concentration in the atmosphere. There are many sources of trace components in the atmosphere, which can be divided into different categories, such as geochemical, biological and human or anthropogenic sources. We will have a look at some few constituents in the atmosphere.

Particulates, ions and radicals

Particulates and aerosols

Particulates and aerosols are very important constituents of the atmosphere. They are small sized solid and liquid matter suspended in the atmosphere of the earth. Particulates include dust, dirt, soot, smoke, and tiny particles of pollutants.

Inorganic sources of particulate matter and aerosols

Wind-blown mineral dust, which comes from mineral oxides, and sea sprays form huge amounts of particulates in the atmosphere.

Metal oxides form a major group of inorganic particles in the atmosphere. They originate from fuel combustion. Iron oxide particles, for example, originate in the combustion of pyrite (Iron disulphide) containing coal. Calcium oxide particles also come from coal combustion. Part of the $CaCO_3$ in the ash fraction of coal is converted to calcium oxide and discharged through the stack.

$$3FeS_2 + 8O_2 \xrightarrow{Heat} Fe_3O_4 + 6SO_2$$

$$CaCO_3 \xrightarrow{Heat} CaO + CO$$

Combustion of leaded gasoline (C_{11}-C_{17} of crude oil) in automobiles releases lead and lead halide particles in the exhaust.

Colloidal sized solid and liquid matters present in the earth's atmosphere are known as aerosols. Global aerosol is mainly from sea salt and consists mainly of sodium chloride originating directly from the ocean (sea spray). These NaCl crystals from the oceans are hygroscopic and under humid conditions they attract water and form a concentrated solution droplet or aerosol. Ultimately, this process can take part in cloud formation. The droplets can also be a site for important chemical reactions in the atmosphere. If strong acids in the atmosphere, perhaps nitric acid (HNO_3) or sulphuric acid (H_2SO_4), dissolve in these small droplets, hydrogen chloride (HCl) can be formed. It is thought that this process is an important source of HCl in the atmosphere:

$$\mathrm{H_2SO_{4(in\ aerosol)}} + \mathrm{NaCl_{(in\ aerosol)}} \rightarrow \mathrm{HCl_{(g)}} + \mathrm{NaHSO_{4(in\ aerosol)}}$$

Aerosol mists are also formed from sulphuric acid, which in turn is obtained by oxidation of sulphur dioxide which collects vapour to form small liquid droplets.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

In the presence of basic air pollutants such as ammonia or calcium oxide, salts are formed.

$$H_2SO_4 + 2NH_3 \rightarrow (NH_3)_2SO_4$$
$$H_2SO_4 + CaO \rightarrow CaSO_4 + H_2O$$

Biological/Geochemical sources of particulates

The particles which occur naturally in the atmosphere are bacteria, fog, pollen and volcanic ash.

Volcanoes are a large source of dust and particularly powerful eruptions can push dust into the stratosphere. It has long been known that volcanic particles can change global temperature by blocking out sunlight. They can also perturb the chemistry at high altitudes. Along with the dust, volcanoes are huge sources of gases such as sulphur dioxide (SO_2), CO_2, HCl and hydrogen fluoride (HF). These gases can react in the stratosphere to provide a further source of particles, with H_2SO_4 being the most important particle produced indirectly from volcanoes.

Incoming meteors also inject particles into the upper atmosphere, which start a series of chemical reactions.

Organic sources of particulates

Organic particulate matter is organic in nature and is obtained from number of sources such as emission from vegetation, automobiles, combustion of fuels etc. One class of components of organic particulate matter, polycyclic aromatic hydrocarbons (PAH) have carcinogenic effect. They originate from the pyrolysis (decomposition brought about by high temperatures) of higher paraffin's present in fuels and plant material. The PAH compounds are usually adsorbed on soot particles. Soot is produced on combustion of fuel in automobiles and thermal power plants. In urban areas it accounts for half of the total particulate load. Soot acts as a carrier for toxic organics due to its large surface area.

Physical and Chemical Properties of Particulate Matter (PM)

- The size and shape of particles comes under physical properties. These particles include liquid droplets, regular or irregular shaped crystals or aggregates of odd shape. Particles are often classified by size, e.g. the particles having diameter less than and up to 10µm are named as PM10 and PM2.5 refers to those of diameter up to 2.5µm.
- The chemical composition of these particles varies a lot. They can be dilute water solution of acids or salts or can be organic liquids and even materials present in the earth's crust (dust) or soot (unburned carbon) and even toxic metals.

Effects of Particulate Matter

- They affect the atmosphere by forming cloud and fog
- They help in balancing the temperature of the atmosphere on earth through light reflection. When particulates reflect light back to outer space, the temperatures are decreased and when they absorb longwave radiation emitted by the earth, they increase the temperatures.
- They serve as nuclei for the development of ice crystals and water droplets.
- They provide a surface for many atmospheric reactions like neutralization of water

droplets, oxidation reactions.

- The health impacts of particulate matter depend on the level of exposure and the duration of exposure. Individual sensitivity to the health impacts of particulate matter can vary as well. Particulate matter is responsible for having adverse effects on human health, especially fine particles such as PM10 and PM2.5, which enter the human body through the respiratory tract.
  - Short-term exposure to particulate matter (or PM) is likely to cause acute health reactions such as irritation to the eyes, nose, and throat, coughing, wheezing and increased frequency of acute lower respiratory infections, deep into the lungs.
  - More prolonged and continued exposure to either high or lower levels of PM10 can give rise to chronic respiratory diseases such as bronchitis, bronchial asthma, pulmonary oedema, ischaemic heart disease, stroke, lung cancer and premature death.
  - PM2.5 is more dangerous than PM10 as they can affect the exchange of gases inside the lungs by reaching the peripheral regions of bronchioles when inhaled. Such symptoms are a particular concern in rural and periurban settings where use of wood, agricultural waste and animal dung is used for cooking, heating and lighting and exposure levels can be high and prolonged over long periods of time.

Ions and radicals in the atmosphere

The upper atmosphere has significant levels of electrons and positive ions

$(e.g, O_2^+, O^+, NO^+, e.t.c.)$ and ultraviolet radiation is primarily responsible for the production of ions in this region. Because of the rarefied conditions, these ions may exist in the atmosphere for long periods before recombining to form neutral species. These ions are prevalent at altitudes of approximately 50 km and above and hence this region is called ionosphere.

Besides ions, free radicals are generated by electromagnetic radiation. They consist of atoms or group of atoms with unpaired electrons. The upper atmosphere is so rarefied that at very high altitudes, radicals may have half-lives of several minutes, or even longer. Radicals can take part in chain reactions in which one of the products of each reaction is a radical. Eventually, through processes such as reaction with another radical, one of the radicals in a chain is destroyed and the chain ends. Free radicals play an important role in photochemical smog formation.

A totally isolated free radical or atom would be quite stable. Therefore, free radicals and single atoms from diatomic gases tend to persist under the rarefied conditions of very high altitudes because they can travel long distances before colliding with another reactive species.

Reactions involving hydroxyl and hydroperoxyl radicals:

A variety of radical species are encountered in the atmospheric chemical reactions. The most important and highly reactive radical species among them is the hydroxyl free radical (•OH). It plays a central role in many atmospheric chemical reactions. It is formed in the troposphere by a variety of means but the most important is a four step process (including two photochemical steps):

The first step involves the breakdown of NO_2:

$$\boldsymbol{NO_2 + h\upsilon \rightarrow NO + O}$$

The formation of O_3 takes place as represented in the equation below in the presence of a third body M, which is mostly N_2 or O_2, which are the most common species.

$$\boldsymbol{O + O_2 + M \rightarrow O_3 + M}$$

Ozone undergoes photolysis in the troposphere as per the following equation:

$$\boldsymbol{O_3 + h\upsilon \rightarrow O^* + O_2}$$

A fraction of the excited (O*) oxygen react with water molecules to give rise to hydroxyl radicals.

$$\boldsymbol{O^* + H_2O \rightarrow 2\ \cdot OH}$$

Hydroxyl radicals are also formed in the atmosphere by the photolysis of H_2O.

$$\boldsymbol{H_2O + h\upsilon \rightarrow \cdot\ OH + \cdot\ H}$$

Hydroxyl radical has short residence time as it is the most frequently removed from the troposphere by reaction with carbon monoxide:

$$\boldsymbol{\cdot OH + CO \rightarrow CO_2 + \cdot\ H}$$

Or with NO_2 leading to the formation of HNO_3, an important contributor to acid rain.

$$\boldsymbol{\cdot OH} + NO_2 \rightarrow HNO_3$$

Or with methane

$$\boldsymbol{CH_4 + \cdot\ OH \rightarrow H_3C\cdot + H_2O}$$

The highly reactive methyl radical $H_3C\cdot$ reacts with O_2

$$\boldsymbol{H_3C\cdot + O_2 + M \rightarrow H_3COO\cdot + M}$$

to form methyl peroxyl radical, $H_3COO\cdot$

Hydrogen radicals produced in the reactions above react with O_2 to produce hydroperoxyl radical an intermediate in some important chemical reactions:

$$H\cdot + O_2 + M \rightarrow HOO\cdot + M(Third\ body)$$

The hydroperoxyl radical can undergo chain termination reactions, such as:

$$HOO\cdot + HO\cdot \rightarrow H_2O + O_2$$

$$HOO. + HOO. \rightarrow H_2 + O_2$$

or reactions that regenerate hydroxyl radical:

$$HOO\cdot + NO \rightarrow NO_2 + HO\cdot$$

$$HOO\cdot + O_3 \rightarrow 2O_2 + HO\cdot$$

The CFCs (chlorofluorocarbons, used in refrigerants and aerosol propellants) have very limited reactivity with OH radical. Gases like these build up in the atmosphere and eventually leak across the tropopause into the stratosphere. Here a very different chemistry takes place, no longer dominated by OH but by reactions which involve atomic oxygen (i.e. O). Gases that react with atomic oxygen in the stratosphere can interfere with the production of O_3:

$$O_{(g)} + O_{2(g)} \rightarrow O_{3(g)}$$

and can be responsible for the depletion of the stratospheric O_3 layer. This means that CFCs are prime candidates for causing damage to stratospheric O_3.

Chemical and photochemical reactions in the atmosphere

Nitrogen and oxygen are the major atmospheric gases and other gases such as argon and carbon dioxide are in minor amounts. Water vapour is also present in the atmosphere in wet air. According to the kinetic molecular theory of gases, the molecules present in the atmosphere are moving and colliding together continuously. In the day time, solar radiations are continuously delivered to the atmosphere. As a result, the molecules present in the atmosphere absorb the light energy and photochemical reactions take place, which would not occur under normal atmospheric temperatures, without light. To determine the nature of chemical species (including pollutant species) in the atmosphere, photochemical reactions play a crucial role.

Reactions involving NO_X

Nitrogen dioxide, NO_2, present in air is known to be photochemically active due to the presence of an unpaired electron. Nitrogen compounds are deposited in the atmosphere by the exhausts of commercial supersonic aircraft flying at high altitude, biological processes e.g N_2O formation by bacteria and combustion activities.

NO_2 molecule reaches a higher level of energy when it absorbs a photon of light with energy hν, which converts the ground state molecule to electronically excited state molecule (designated by an asterisk *).

$$\boldsymbol{NO_2} + \boldsymbol{h}\upsilon \rightarrow \boldsymbol{NO_2}^*$$

The excited molecule, NO_2* may quickly re-emit a photon of light,

$$\boldsymbol{NO_2}^* \rightarrow \boldsymbol{NO_2} + \boldsymbol{h}\upsilon$$

Alternatively, photodissociation may occur, i.e., when energy results in breaking of N – O bond and produces a nitrogen monoxide (NO) molecule and an oxygen atom (O).

$$\boldsymbol{NO_2} + \boldsymbol{h}\upsilon \rightarrow \boldsymbol{NO} + \boldsymbol{O}$$

Both of them are free radicals, as they contain unpaired electrons.

Chemical species in the atmosphere excited due to absorption of light may also undergo photoionization through loss of an electron:

$$\boldsymbol{N_2^*} \rightarrow \boldsymbol{N_2^+} + \boldsymbol{e^-}$$

Reactions involving O_X

Photodissociation of molecular oxygen results in two oxygen atoms.

$$O_2 \rightarrow O + O$$

Oxygen atoms are free radicals, which immediately react with another atom or molecule.

An excited species may also react directly with another species:

$$O_2^* + O_3 \rightarrow 2O_2$$

Other phenomena undergone by excited chemical species may be intermolecular energy transfer or intramolecular energy transfer:

$$N_2^* + O_2 \rightarrow N_2^+ + O_2^*$$

$$XY^* \rightarrow XY^§$$

Here, $XY^§$ is another excited state of the same molecule.

The urban atmosphere

How do human activities influence the atmosphere? The changes wrought by humans are important, though often subtle on the global scale. It is in the urban atmosphere where human influence shows its clearest impact, so it is necessary to treat the chemistry of the urban atmosphere as a special case. In urban environments there are pollutant compounds emitted to the atmosphere directly and these are called primary pollutants. Smoke is the archetypical example of a primary pollutant. However, many compounds undergo reactions in the atmosphere and the products of such reactions are called secondary pollutants. Thus, many primary pollutants can react to produce secondary pollutants. It is the distinction between primary and secondary pollution that now governs our understanding of the difference between two quite distinct types of air pollution that affect major cities of the world.

Smog Formation

The term smog is formed by the combination of two words, smoke and fog. Smog is basically of two types: industrial smog (or London smog) and photochemical smog (or Los Angeles smog).

London Smog- Primary pollutants

The Industrial smog is also called the London smog since London is the place of origin of the Industrial Revolution and it was the first place to experience occurrences of smog. In the worst reported smog incident – which occurred in 1952, around four thousand people were killed.

Fuels usually consist of hydrocarbons, except in particularly exotic applications such as rocketry, where nitrogen, aluminium (Al) and even beryllium (Be) are sometimes used. Normal fuel combustion is an oxidation reaction and can be described:

$$\text{'4CH'} + 5O_{2(g)} \rightarrow 4CO_{2(g)} + 2H_2O_{(g)}$$
$$\text{fuel + oxygen} \rightarrow \text{carbon dioxide + water}$$

Neither CO_2 nor water is particularly toxic, however, with less O_2 during combustion, i.e. as might occur inside an engine or boiler, the equation might now be written:

$$\text{'4CH'} + 3O_{2(g)} \rightarrow 4CO_{(s)} + 2H_2O_{(g)}$$
$$\text{coal + oxygen} \rightarrow \text{carbon monoxide + water}$$

Here we have produced carbon monoxide (CO), a poisonous gas. With even less oxygen we can get carbon (i.e. smoke):

$$\text{'4CH'} + O_{2(g)} \rightarrow 4C_{(s)} + 2H_2O_{(g)}$$
coal + oxygen → 'smoke' + water

At low temperatures, in situations where there is relatively little O_2, pyrolysis reactions (i.e. reactions where decomposition takes place as a result of heat) may cause a rearrangement of atoms that can lead to the formation of polycyclic aromatic hydrocarbons during combustion which are carcinogenic. In addition to these problems, fossil fuels have impurities e.g sulphur (S), partly present as the mineral pyrite, FeS_2. There may be as much as 6% sulphur in some coals and this is converted to SO_2 on combustion:

$$4FeS_{2(s)} + 11O_{2(g)} \rightarrow 8SO_{2(g)} + 2Fe_2O_{3(s)}$$

SO_2 and smoke came to epitomize the traditional air pollution problems of cities. Smoke and SO_2 are obviously primary pollutants because they are formed directly at a clearly evident pollutant source and enter the atmosphere in that form.

Classical air pollution incidents in London occurred under damp and foggy conditions in the winter. Fuel use was at its highest and the air near-stagnant. The presence of smoke and fog together led to the invention of the word smog (sm[oke and f]og), now often used to describe air pollution in general. Most of the air pollutants in here came from stationary sources e.g boilers, furnaces (and traditionally steam engines), domestic chimneys, steam turbines and power stations.

Sulphur dioxide is fairly soluble so could dissolve into the water that condensed around smoke particles.

$$SO_{2(g)} + H_2O_{(l)} \leftrightharpoons H^+_{(aq)} + HSO^-_{3(aq)}$$

Traces of metal contaminants (iron (Fe) or manganese (Mn)) catalysed the conversion of dissolved SO_2 to H_2SO_4

$$2HSO^{-}_{3(aq)} + O_{2(aq)} \rightarrow 2H^{+}_{(aq)} + 2SO^{2-}_{4(aq)}$$

Sulphuric acid has a great affinity for water so the droplet absorbed more water. Gradually the droplets grew and the fog thickened and that is why smog in London is also known as sulphurous smog. Terrible fogs plagued London at the turn of the last century and incidences of bronchial diseases increased.

Los Angeles smog—secondary pollution

The transition from coal derived fuels to petroleum-derived fuels this century has seen the emergence of an entirely new kind of air pollution. This newer form of pollution is the result of the greater volatility of liquid fuels. The motor vehicle is such an important consumer of liquid fuels that it has become a major source of contemporary air pollution. However, the pollutants really responsible for causing the problems are not themselves emitted by motor vehicles. Rather, they form in the atmosphere. These secondary pollutants are formed from the reactions of primary pollutants, such as NO and unburnt fuel, which come directly from the automobiles. Chemical reactions that produce the secondary pollutants proceed most effectively in sunlight, so the resulting air pollution is called photochemical smog.

Photochemical smog was first noticed in Los Angeles during the Second World War. Initially it was assumed to be similar to the air pollution that had been experienced elsewhere, but conventional smoke abatement techniques failed to lead to any improvement. In the 1950s it was realized that the smog was caused by reactions of automobile exhaust vapours in sunlight.

Fuels are not burned in O_2, but in air which is a mixture of O_2 and N_2. At high temperature, in a flame, molecules in air may fragment, and even the relatively inert N_2 molecule can undergo reaction:

$$O_{(g)} + N_2 \rightarrow NO_{(g)} + N_{(g)} \quad (i)$$

$$N_{(g)} + O_{2(g)} \rightarrow NO_{(g)} + O_{(g)} \quad (ii)$$

Equation (ii) produces an oxygen atom, which can re-enter equation (i). Once an oxygen atom is formed in a flame, it will be regenerated and contribute to a whole chain of reactions that produce NO. If we add these two reactions we get:

$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)} \quad (iii)$$

The equations show how nitrogen oxides are generated in flames. They arise because we burn fuels in air rather than just in O_2. In addition, some fuels contain nitrogen compounds as impurities, so the combustion products of these impurities are a further source of nitrogen oxides (i.e. NOx, the sum of NO and NO_2).

Oxidation of nitric oxide in smog gives nitrogen dioxide, which is a brown gas.

$$\mathbf{2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}\ (iv)}$$

This colour means that it absorbs light and is photochemically active and undergoes dissociation:

$$\mathbf{NO_{2(g)} + hv \rightarrow NO_{(g)} + O_{(g)}}\ \text{(v)}$$

Equation (v) thus reforms the nitric oxide, but also gives an isolated and reactive oxygen atom, which can react to form O_3:

$$\mathbf{O_{(g)} + O_{2(g)} \rightarrow O_{3(g)}\ (vi)}$$

Ozone is the single pollutant that most clearly characterizes photochemical smog. However, O_3, which we regard as such a problem, is not emitted by automobiles (or any major polluter). It is a secondary pollutant. It can also react with NO to form NO_2 and O_2:

$$O_{3(g)} + NO_{(g)} \rightarrow NO_{2(g)} + O_{2(g)}$$

The volatile organic compounds released through the use of petroleum fuels also serve to aid the

conversion of NO to NO_2. The reactions are quite complicated, involving several elementary steps but we can simplify them by using a very simple organic molecule such as CH_4, to represent the petroleum vapour from vehicles:

$$CH_{4(g)} + 2O_{2(g)} + 2NO_{(g)} \xrightarrow{h\nu} H_2O_{(g)} + HCHO_{(g)} + 2NO_{2(g)}$$

This equation simply shows the net reaction in photochemical smog. We can see two things taking place in this reaction. Firstly, the automobile hydrocarbon is oxidized to an aldehyde (i.e. a molecule with a CHO functional group). In the reaction above it is formaldehyde (HCHO). Aldehydes are eye irritants and, at high concentrations, also carcinogens. Further reactions lead to the formation of ketones and peroxy compounds. Ozone, aldehydes, ketones and peroxy (e.g peroxyacetylnitrate (PAN)) compounds so formed are thus secondary air pollutants.

There is no fog when Los Angeles smog forms, and visibility does not decline to just a few metres, as was typical of London fogs. Of course, the Los Angeles smog forms best on sunny days. London fogs are blown away by wind, but the gentle sea breezes in the Los Angeles basin can hold the pollution in against the mountains and prevent it from escaping out to sea. The pollution cannot rise in the atmosphere because it is trapped by an inversion layer: the air at ground level is cooler than that aloft, so that a cap of warm air prevents the cooler air from rising and dispersing the pollutants. A fuller list of the differences between Los Angeles and London-type smogs is given in the table below:

Comparison of Los Angeles and London smog.

Characteristic	Los Angeles	London
Air temperature	24 to 32°C	−1 to 4°C
Relative humidity	<70%	85% (+ fog)
Type of temperature inversion	Subsidence, at 1000 m	Radiation (near ground) at a few hundred metres
Wind speed	<3 m s^{-1}	Calm
Visibility	<0.8–1.6 km	<30 m
Months of most frequent occurrence	Aug. to Sept.	Dec. to Jan.
Major fuels	Petroleum	Coal and petroleum products
Principal constituents	O_3, NO, NO_2, CO, organic matter	Particulate matter, CO, S compounds
Type of chemical reaction	Oxidative	Reductive
Time of maximum occurrence	Midday	Early morning
Principal health effects	Temporary eye irritation (PAN)	Bronchial irritation, coughing (SO_2/smoke)
Materials damaged	Rubber cracked (O_3)	Iron, concrete

Effects of London Smog

- Smoke causes black incrustations buildings, soils clothes and blacken curtains, hangings and trees
- Affects plant growth
- Plants are also very sensitive to SO_2 and one of the first effects seems to be the inhibition of photosynthesis.

- The traditional smog generated by coal burning contained SO_2 and its oxidation product, H_2SO_4. Sulphuric acid is a powerful corrosive agent and rusts iron bars and weathers building stones through the reaction:

$$H_2SO_{4(aq)} + CaCO_{3(s)} + H_2O_{(l)} \rightarrow CO_{2(g)} + CaSO_{4(s)}.2H_2O_{(l)}$$

  Sulphuric acid converts limestone ($CaCO_3$) into gypsum ($CaSO_4.2H_2O$). The deterioration is severe because gypsum is soluble and dissolves in rain. Perhaps more importantly, gypsum occupies a larger volume than limestone, which adds mechanical stress so that the stone almost explodes from within.

Effects of photochemical smog

All the major constituents of photochemical smog are detrimental to human health and the environment. Being a cocktail of chemical oxidants such as ozone, nitrogen dioxide and peroxy compounds, it is often termed as oxidizing smog.

- The brown nitrogen dioxide in smog affects visibility.
- Nitrogen dioxide, ozone, VOCs and peroxyacetyl nitrates, all result in eye irritation and respiratory problems.
- Prolonged exposure to NO_2 lowers resistance towards respiratory infections.
- Nitrogen oxides have the following effects:
    - May increase cases of cancer
    - Form acid rain which can harm plants and animals by increasing the efficiency of production of H_2SO_4 on stone surfaces in those cities that have moderate SO_2 concentrations.

$$H_2SO_{4(aq)} + CaCO_{3(s)} + H_2O_{(l)} \rightarrow CO_{2(g)} + CaSO_{4(s)}.2H_2O_{(l)}$$

- Ozone has a harsh odour and causes coughing, wheezing and eye irritation.
- Ozone causes oxidative damage to plant and animal tissue. It may also attack the double bonds of organic molecules e.g rubber is degraded and cracked by O_3. Many pigments and dyes are also attacked by O_3. The usual result of this is that the dye fades. Ozone damages plants by changing the 'leakiness' of cells to important ions such as potassium. Early symptoms of such injury appear as water-soaked areas on the leaves.
- Some VOCs are also carcinogenic.
- Peroxy compounds causes irritation in eye and respiratory problems. It is considered to be more toxic than ozone for plants.

Factors Affecting the Formation of Photochemical Smog-:

There are several factors that affect the formation of photochemical smog:

- Locality with a higher number of industries and automobiles. High concentrations of nitrogen oxides and volatile organic compounds are associated with automobile exhausts and emissions from industry where this combination of substances arises due to fossil fuel combustion.
- The concentration of photochemical smog present in atmosphere varies with "the time of day". As the traffic in early morning increases, the concentrations of nitrogen oxides and VOCs also increase. But as the traffic decreases later in the morning, the reaction between nitrogen oxides and volatile organic compounds takes place and nitrogen dioxide is formed which results in increase in its concentration. Around

noon, the intensity of sunlight is high and it results in breakdown of nitrogen dioxide and formation of ozone. At the same time, some of the nitrogen dioxide can react with the volatile organic compounds to form Peroxy compounds and other toxic chemicals. As the sun goes down, the production of ozone and Peroxy compounds ceases. There are several reactions, which result in consumption of the ozone and other oxidants present in the atmosphere.

- There are many meteorological factors affecting the formation of photochemical smog. Rain can dissipate photochemical smog as the pollutants are rinsed out of the atmosphere with rainfall. Photochemical smog can be blown away by wind and resulting in replacement by fresh air. However, temperature inversion can cause increase in the impact of photochemical smog. Normally, during the day, air, which is near the earth's surface, is warmed and rises up, carrying pollutants with it. However, a temperature inversion traps pollutants near the surface of the earth. A temperature inversion is a phenomenon in which the normal tropospheric decrease in temperature with height changes to increase in temperature with increasing height. A temperature inversion thus traps a layer of cold air beneath warm air, reducing mixing of the atmosphere due to convection. Dispersion of pollutants, therefore, decreases. Inversions can remain in place for some days, which may stretch to several weeks. They are usually caused by several factors including when the air near the ground rapidly loses its heat on a clear night. The ground becomes cooled quickly while the air above it retains the heat the ground was holding during the day. They may also occur in coastal areas because upwelling of cold water can decrease surface air temperature and the cold air mass stays under warmer ones.

- Topography also affects a smog event. Towns located in valleys are more affected by photochemical smog because the surrounding hills and mountains reduce airflow, allowing the amounts of pollutants to rise. Valleys are also sensitive to photochemical smog because there is a stronger tendency for temperature inversion to take place in valleys since it can sometimes cause cold air to flow from mountain peaks down into valleys. The cold air then pushes under the warm air rising from the valley, creating an inversion.

Mitigation Measures for Photochemical Smog

[1] Catalytic converters

Smog formation could be reduced if the amounts of oxides of nitrogen and hydrocarbons released in the atmosphere decrease. This is done by installing efficient catalytic converters in automobiles. A two-way catalytic converter, consisting of a mixture of platinum and palladium supported on a ceramic or metal honeycomb bed, removes hydrocarbons and carbon monoxide from the exhaust. It is an oxidation catalyst, which converts CO to CO_2 and hydrocarbons to CO_2 and water when the exhaust gases are forced through it.

$$2CO + O_2 \xrightarrow{CATALYST} 2CO_2$$

$$RH(Hydrocarbons) + O_2 \xrightarrow{Catalyst} CO_2 + H_2O$$

A three-way catalytic converter consisting of a mixture of platinum, palladium and rhodium deposited on a high surface area ceramic and metal honeycomb or alumina pellets removes hydrocarbons, carbon monoxide and nitrogen oxides from the exhaust. The converter contains an oxidation- reduction catalyst mixture. Hydrocarbons and carbon monoxide are oxidized while nitrogen oxides are reduced. In the exhaust system the nitric oxide reacts with carbon monoxide to give nitrogen and carbon dioxide:

$$2CO + 2NO \xrightarrow{catalyst} N_2 + 2CO_2$$

NOx and hydrocarbons interact to give nitrogen, carbon dioxide and water:

$$NO_x + RH \xrightarrow{catalyst} N_2 + CO_2 + H_2O$$

[2] Free radical traps-:

Certain compounds can act as free radical traps i.e., when sprayed in the atmosphere; they result in production of free radicals that readily combine with free radical initiators of photochemical smog (such as $O^{\cdot}$, $R^{\cdot}$, $RO^{\cdot}$, $H^{\cdot}$ etc.). The introduction of such compounds will slow down the conversion of NO to NO_2 from the usual 2-6 hours to 6-12 hours. Thus, the conversion will take place around the time of sunset and photochemical decomposition of nitrogen dioxide, which is the smog initiation step, would be inhibited.

[3] Petrol reformulation-:

Summer petrol used in some European countries is a reformulated gasoline in which 1/10 of the aromatic hydrocarbons have been replaced by oxygenated fuel such as methyl tertiary butyl ether. These additives allow more complete and efficient combustion, thus suppressing the emission of volatile organic compounds. The emission of nitrogen oxides is reduced since petrol containing oxygenates burns at a lower temperature. Decreased emission of VOCs and nitrogen oxides suppresses smog formation.

[4] Alternative energy sources-:

Hybrid cars, hydrogen fueled cars, electric cars and cars run on different types of biodiesel may be viable methods of cutting down on vehicular exhaust emissions in the near future.