

## 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

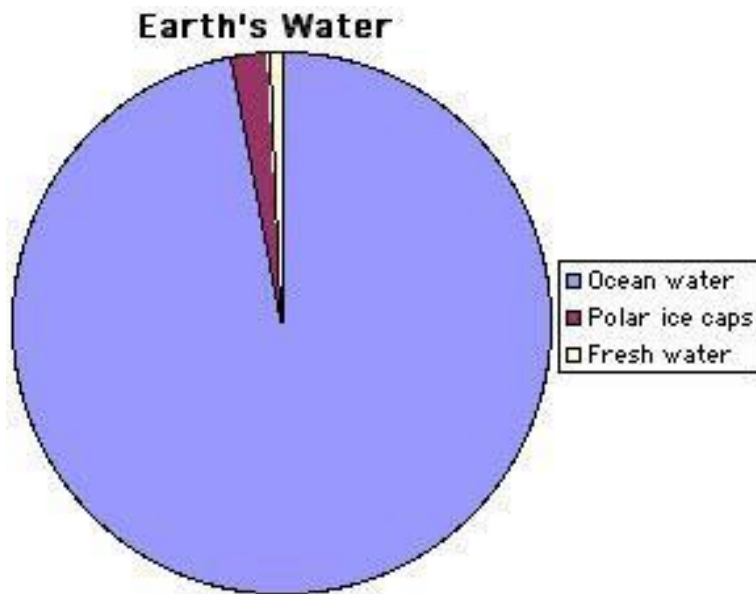
the earth and thus controls the temperature of the earth through heat retention, making possible a comfortable mean temperature of  $\pm 15^{\circ}\text{C}$ .

- 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  $\text{km}^3$ . 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:

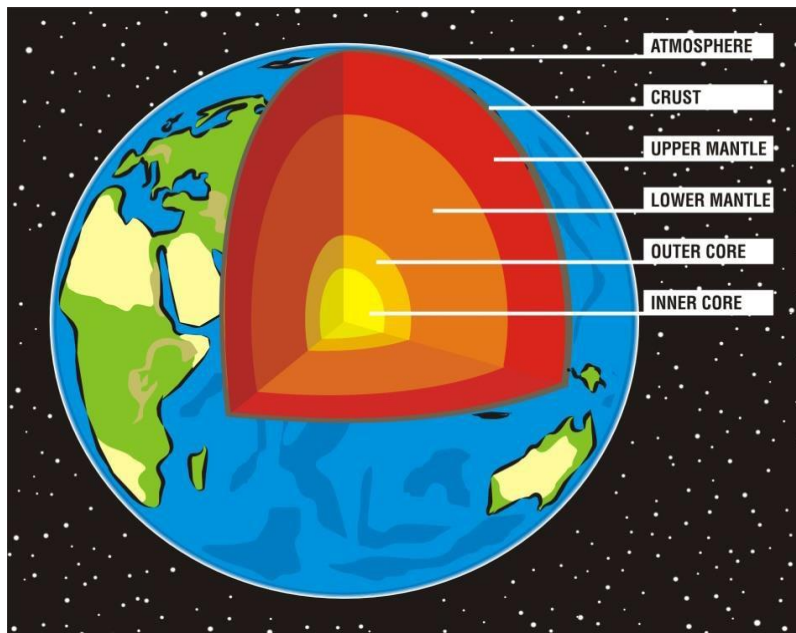


The extent of the use of available fresh water for various purposes is dependent on the locality.

The major problem with global water supply is its 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:



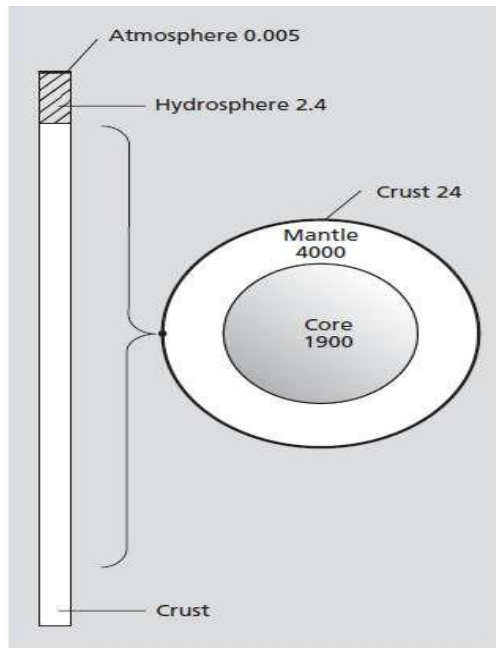
- The lithosphere consists of the **upper mantle** and **the crust**.
- The crust is the earth's outer skin that is accessible to human. The crust consists of rocks and soil of which the latter is the important part of lithosphere.

## 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 disperse 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.

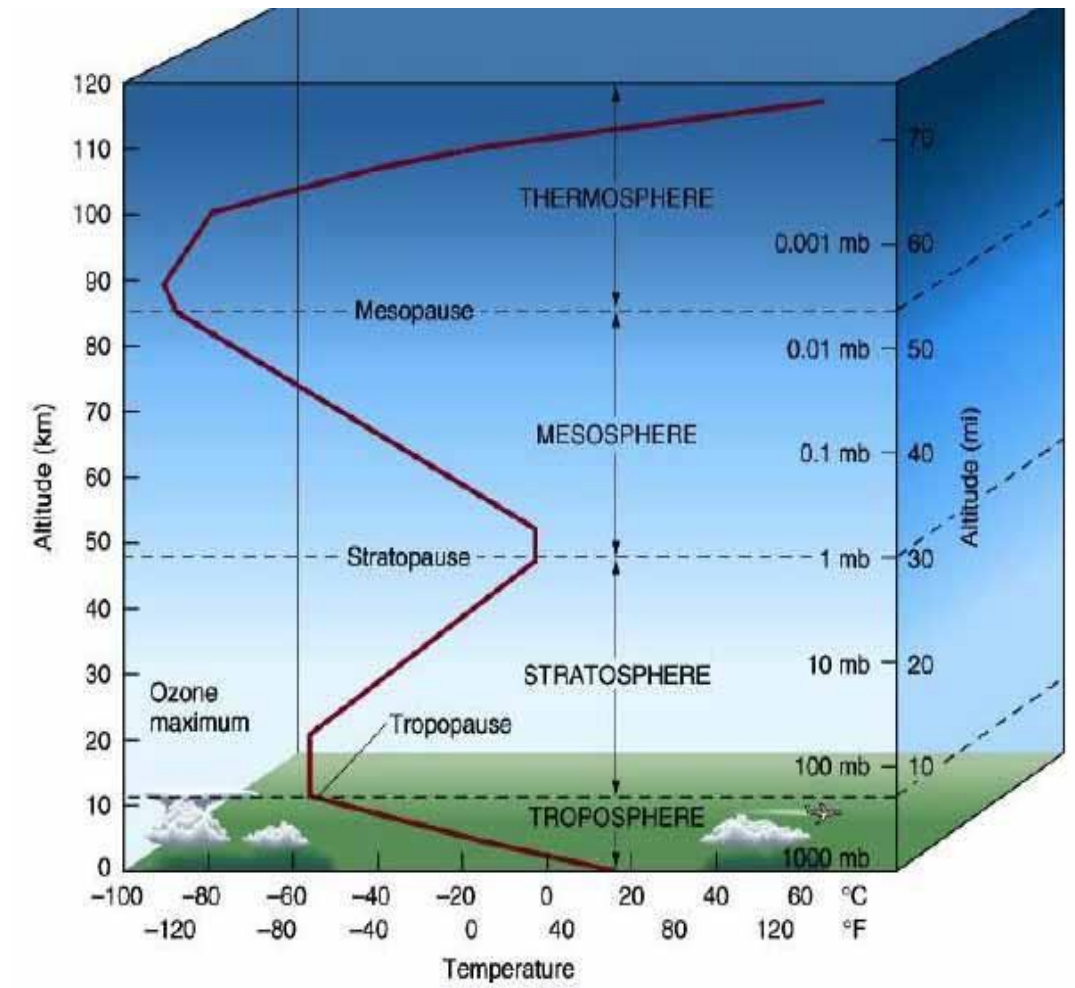
Maximum atmosphere is located close to the surface, within 16 kilometres. Though the atmosphere extends into outer space and there is no distinct border between them, but an imaginary line called the Kármán Line which is approximately at the height of 100 km is called as the boundary of Earth's atmosphere.

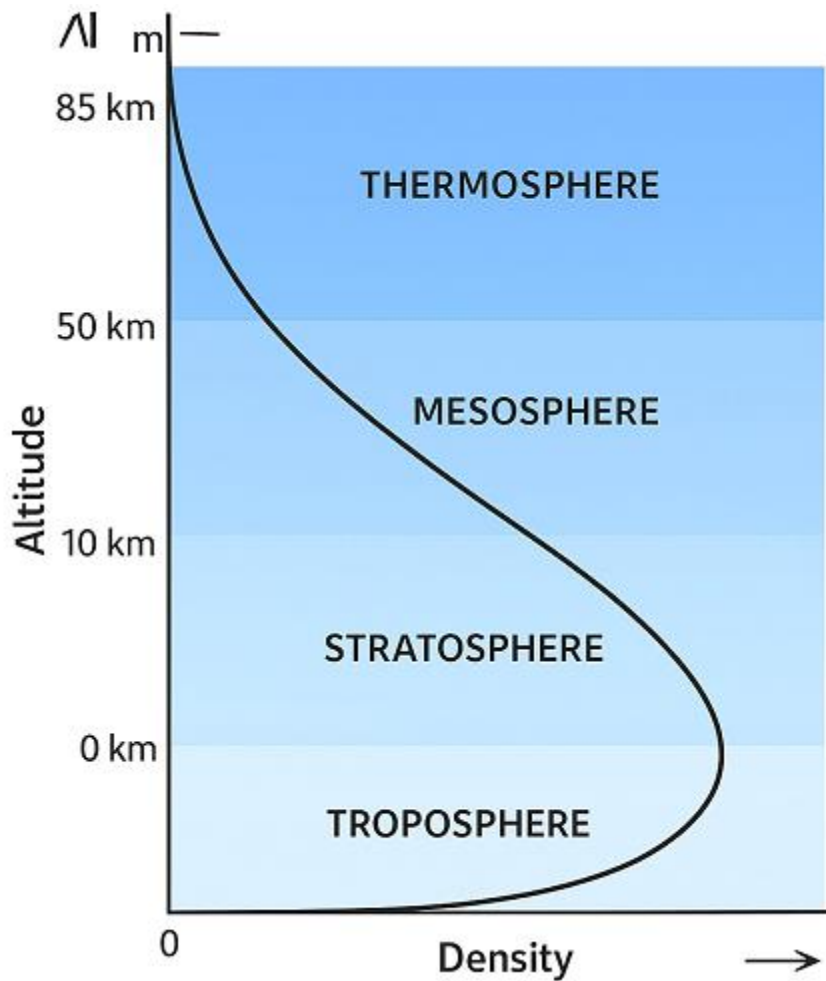
### Composition of the Atmosphere

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  $6.5^{\circ}\text{C}$  per km as the altitude increases.

The average temperature near the surface is  $15^{\circ}\text{C}$  while it is  $-57^{\circ}\text{C}$  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.

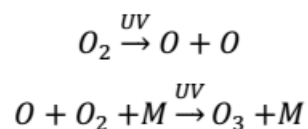
Approximately 99% of the atmosphere is located up to this height, which includes almost all the gases. Weather balloons and jet aircrafts fly in this region, as the air present in this layer is very thin. This increases the fuel efficiency of the aircrafts.

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.

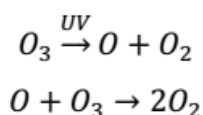
Ozone – which is a mainly formed from photochemical smog – is considered to be dangerous for health if it reaches the ground level or near the surface of the earth.

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:



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:



This process is called the Chapman cycle and M is a third body, which could be a random air molecule (O<sub>2</sub> or N<sub>2</sub>).

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 'miso' 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  $-100^{\circ}\text{C}$ . This is due to the absence of high levels of radiation absorbing species, particularly ozone. The principal chemical species in this region are  $\text{O}_2^+$  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<sub>2</sub> 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<sub>2</sub> 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

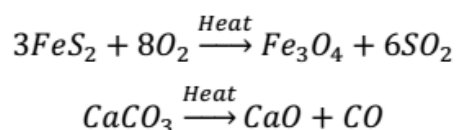
#### Particulates and aerosols

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

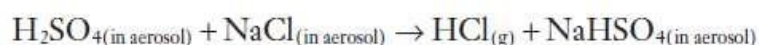
Wind-blown mineral dust, which comes from mineral oxides, and sea sprays form huge amounts of particulates in the atmosphere.

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  $\text{CaCO}_3$  in the ash fraction of coal is converted to calcium oxide and discharged through the stack.

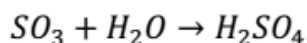
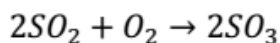


Combustion of leaded gasoline ( $\text{C}_{11}$ - $\text{C}_{17}$  of crude oil) in automobiles releases lead and lead halide particles in the exhaust.

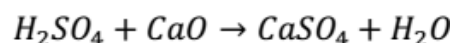
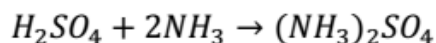
Colloidal sized solid and liquid matters present in the earth's atmosphere are known as aerosols. Global aerosol is mainly from sea salt and consists mainly of sodium chloride originating directly from the ocean (sea spray). These NaCl crystals from the oceans are hygroscopic and under humid conditions 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 ( $\text{HNO}_3$ ) or sulphuric acid ( $\text{H}_2\text{SO}_4$ ), 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:



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.



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



### 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<sub>2</sub>), CO<sub>2</sub>, HCl and hydrogen fluoride (HF). These gases can react in the stratosphere to provide a further source of particles, with H<sub>2</sub>SO<sub>4</sub> 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  $10\mu\text{m}$  are named as PM<sub>10</sub> and PM<sub>2.5</sub> refers to those of diameter up to  $2.5\mu\text{m}$ .
- 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.

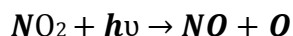
- They serve as nuclei for the development of ice crystals and water droplets.
- They provide a surface for many atmospheric reactions like neutralization of water droplets, oxidation reactions.
- The health impacts of particulate matter depend on the level of exposure and the duration of exposure. Individual 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 PM<sub>10</sub> and PM<sub>2.5</sub>, 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 PM<sub>10</sub> can give rise to chronic respiratory diseases such as bronchitis, bronchial asthma, pulmonary oedema, ischaemic heart disease, stroke, lung cancer and premature death.
  - PM<sub>2.5</sub> is more dangerous than PM<sub>10</sub> 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.,  $\text{O}_2^+$ ,  $\text{O}^+$ ,  $\text{NO}^+$ , e. t. c.) and ultraviolet radiation is primarily responsible for the production of ions in this region.
- ❖ Because of the rarefied (not dense; thin) 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:*

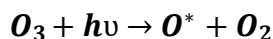
- ❖ A variety of radical species are encountered in the atmospheric chemical reactions.
- ❖ The most important and highly reactive radical species among them is the hydroxyl free radical ( $\cdot\text{OH}$ ). It plays a central role in many atmospheric chemical reactions.
- ❖ It is formed in the troposphere 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  $\text{NO}_2$ :



The formation of  $\text{O}_3$  takes place as represented in the equation below in the presence of a third body M, which is mostly  $\text{N}_2$  or  $\text{O}_2$ , which are the most common species.

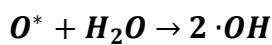


Ozone undergoes photolysis in the troposphere as per the following equation (ozone is a highly reactive and unstable molecule and decomposes into dioxygen when hit by other uv light photons):

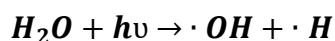


*This last reaction is the main uv screening effect of the upper atmosphere and the ozone absorbs a lot of the harmful incoming uv radiation from the Sun.*

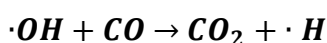
A fraction of the excited ( $\text{O}^*$ ) oxygen react with water molecules to give rise to hydroxyl radicals.



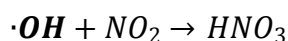
- ❖ Hydroxyl radicals are also formed in the atmosphere by the photolysis of H<sub>2</sub>O.



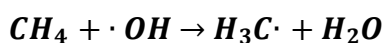
- ❖ Hydroxyl radical has short residence time as it is the most frequently removed from the troposphere by reaction with carbon monoxide:



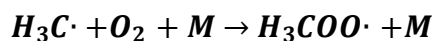
or with NO<sub>2</sub> leading to the formation of HNO<sub>3</sub>, an important contributor to acid rain.



or with methane

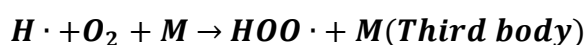


the highly reactive methyl radical H<sub>3</sub>C· reacts with O<sub>2</sub>

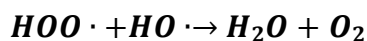


to form methyl peroxy radical, H<sub>3</sub>COO·

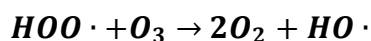
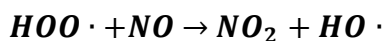
- ❖ Hydrogen radicals produced in the reactions above react with O<sub>2</sub> to produce hydroperoxyl radical an intermediate in some important chemical reactions:



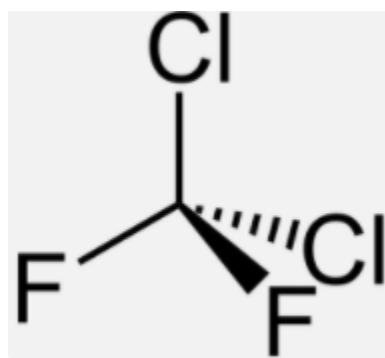
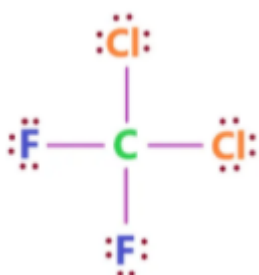
the hydroperoxyl radical can undergo chain termination reactions, such as:



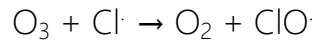
or reactions that regenerate hydroxyl radical:



- ❖ 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<sub>3</sub> and can be responsible for the depletion of the stratospheric O<sub>3</sub> layer. This means that CFCs are prime candidates for causing damage to stratospheric O<sub>3</sub>.
- ❖ The chemically very stable CFCs diffuse up into the stratosphere and decompose when hit by ultraviolet light (uv) to produce free radicals, including free chlorine atoms, which themselves are highly reactive free radicals.
  - e.g.  $\text{CCl}_2\text{CF}_2 \rightarrow \text{CClF}_2\cdot + \text{Cl}\cdot$  (note the C–Cl bond is weaker than the C–F bond, so breaks first)



The formation of chlorine atom radicals is the root of the problem because they readily react with ozone and change it back to much more stable ordinary oxygen.



and then:  $\text{ClO}\cdot + \text{O} \rightarrow \text{Cl} + \text{O}_2$ , (which means the 'destructive' Cl atom free radical is still around)

The two reactions above involving chlorine atoms are known as a catalytic cycle because the chlorine atoms from CFC's etc. act as a catalyst in the destruction of ozone.

- ❖ Therefore many countries are banning the use of CFCs, but not all despite the fact that scientists predict it will take many years for the depleted ozone layer to return to its 'original'  $\text{O}_3$  concentration and alternatives to CFC's are already being marketed.
  - BUT at least the ozone layer is recovering thanks to some world-wide co-operation and the work of chemists in developing less environmentally harmful alternatives.
- ❖ In other parts of stratosphere  $\text{NO}_2$ ,  $\text{CH}_4$  react with  $\text{ClO}^*$  and  $\text{Cl}^*$  respectively and act as natural sink for  $\text{ClO}^*$  and  $\text{Cl}^*$

These reactions consume  $\text{Cl}^*$  and  $\text{ClO}^*$  (hindrance to ozone depletion).

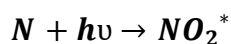
### Chemical and photochemical reactions in the atmosphere

- ❖ 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.

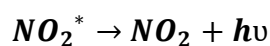
- ❖ According to the kinetic molecular theory of gases, the molecules present in the atmosphere are moving and colliding together continuously. In the day time, solar radiations are continuously delivered to the atmosphere. As a result, the molecules present in the atmosphere absorb the light energy 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<sub>x</sub>

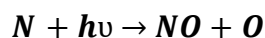
- ❖ Nitrogen dioxide, NO<sub>2</sub>, present in air is known to be photochemically active due to the presence of an unpaired electron.
- ❖ Nitrogen compounds are deposited in the atmosphere by the exhausts of commercial supersonic aircraft flying at high altitude, biological processes e.g N<sub>2</sub>O formation by bacteria and combustion activities.
- ❖ NO<sub>2</sub> molecule reaches a higher level of energy when it absorbs a photon of light with energy  $h\nu$ , which converts the ground state molecule to electronically excited state molecule (designated by an asterisk \*).



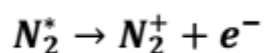
- ❖ The excited molecule, NO<sub>2</sub>\* may quickly re-emit a photon of light,



- ❖ 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).

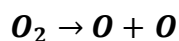


- ❖ Both of them are free radicals, as they contain unpaired electrons.
- ❖ Chemical species in the atmosphere excited due to absorption of light may also undergo **photoionization** through loss of an electron:

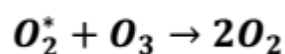


### Reactions involving O<sub>x</sub>

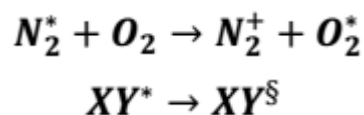
- ❖ Photodissociation of molecular oxygen results in two oxygen atoms.



- ❖ Oxygen atoms are free radicals, which immediately react with another atom or molecule.
- ❖ An excited species may also react directly with another species:



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



- ❖ Here, XY<sup>§</sup> 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

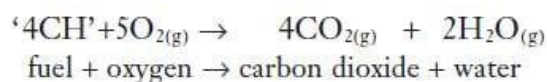
- ❖ The term smog is formed by the combination of two words, smoke and fog. Smog is basically of two types: industrial smog (or London smog) and photochemical smog (or Los Angeles smog).

### *London Smog- Primary pollutants*

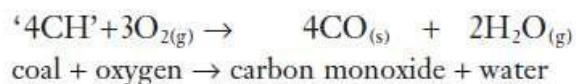
- ❖ The **Industrial smog** is also called the London smog since London is the place of origin of the Industrial Revolution and it was the first place to experience occurrences of

smog. In the worst reported smog incident – which occurred in 1952, around four thousand people were killed.

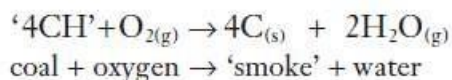
- ❖ Fuels usually consist of hydrocarbons, except in particularly exotic applications such as rocketry, where nitrogen, aluminium (Al) and even beryllium (Be) are sometimes used.
- ❖ Normal fuel combustion is an oxidation reaction and can be described:



- ❖ Neither CO<sub>2</sub> nor water is particularly toxic, however, with less O<sub>2</sub> during combustion, i.e. as might occur inside an engine or boiler, the equation might now be written:

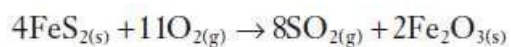


Here we have produced carbon monoxide (CO), a poisonous gas. With even less oxygen we can get carbon (i.e. smoke):

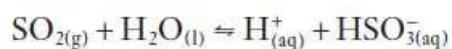


- ❖ At low temperatures, in situations where there is relatively little O<sub>2</sub>, pyrolysis reactions (i.e. reactions where decomposition takes place as a result of heat) may cause a rearrangement of atoms that can lead to the formation of polycyclic aromatic hydrocarbons during combustion which are carcinogenic.

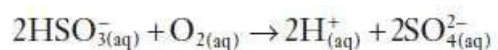
- ❖ In addition to these problems, fossil fuels have impurities e.g sulphur (S), partly present as the mineral pyrite,  $\text{FeS}_2$ . There may be as much as 6% sulphur in some coals and this is converted to  $\text{SO}_2$  on combustion:



- ❖  $\text{SO}_2$  and smoke came to epitomize the traditional air pollution problems of cities. Smoke and  $\text{SO}_2$  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 (smoke and fog), 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.



- ❖ Traces of metal contaminants (iron (Fe) or manganese (Mn)) catalysed the conversion of dissolved  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$



- ❖ 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*

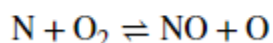
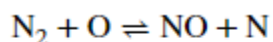
- ❖ The transition from coal derived fuels to petroleum-derived fuels this century has seen the emergence of an entirely new kind of air pollution.
- ❖ This newer form of pollution is the result of the greater volatility of liquid fuels.
- ❖ The motor vehicle is such an important consumer of liquid fuels 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.

- ❖ To fully appreciate photochemical smog formation, one must first recognize that nitrogen is transformed between many different substances in the atmosphere. Automobile exhausts release nitrous oxide (NO) along with small amounts of nitrogen dioxide (NO<sub>2</sub>).
- ❖ The substances that react with nitrogen oxides to form oxidants (the final product of photochemical smog) are trace hydrocarbons (from incomplete combustion) and the hydroxyl radical.
- ❖ The necessary ingredients for photochemical smog formation are (1) nitrogen oxides, (2) sunlight, and (3) hydrocarbons.
- ❖ Combustion is a complex process involving many intermediate steps, not just the single-step reaction shown in a simple overall equation. Fuels are not burned in O<sub>2</sub>, but in air which is a mixture of O<sub>2</sub> and N<sub>2</sub>.
- ❖ The highly energetic environment of a flame causes molecules (fuel and O<sub>2</sub>) to break down into highly reactive atoms and molecular fragments called free radicals (such as O, H, OH, HO<sub>2</sub>).
- ❖ Even the relatively inert N<sub>2</sub> molecule can undergo reaction producing highly reactive nitrogen atoms (radicals) that then react with oxygen.

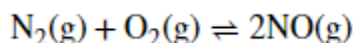
- ❖ The formation of nitrogen oxides at high temperatures (typically above 1300 °C from the nitrogen in the air is known as the thermal NO<sub>x</sub> mechanism or the extended Zeldovich mechanism.

The principal reactions involved are:



Equation (ii) produces an oxygen atom, which can re-enter equation (i).

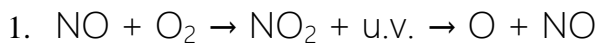
The overall simplified reaction for the formation of nitric oxide is:



The equations show how nitrogen oxides are generated in flames. They arise because we burn fuels in air rather than just in O<sub>2</sub>. 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. NO<sub>x</sub>, the sum of NO and NO<sub>2</sub>).

- ❖ Photochemical smog formation proceeds through a sequence of reactions, all involving a free radical mechanism.

NO <sub>2</sub> (nitrogen dioxide)	+ Sunlight	→ NO (nitric oxide)	+ O (atomic oxygen)
O	+ O <sub>2</sub> (molecular oxygen)	→ O <sub>3</sub> (ozone)	
O <sub>3</sub>	+ NO	→ NO <sub>2</sub>	+ O <sub>2</sub>
O	+ HC (hydrocarbons)	→ HCO• (radical)	
HCO•	+ O <sub>2</sub>	→ HCO <sub>3</sub> •	
HCO <sub>3</sub> •	+ HC	→ Aldehydes and ketones	
HCO <sub>3</sub> •	+ NO	→ HCO <sub>2</sub> •	+ NO <sub>2</sub>
HCO <sub>3</sub> •	+ O <sub>2</sub>	→ O <sub>3</sub>	+ HCO <sub>2</sub> •
HCO <sub>x</sub> •	+ NO <sub>2</sub>	→ Peroxyacetyl nitrates	

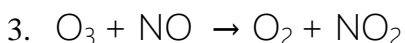


In this first reaction, we start with Nitric Oxide (NO), which we already know is emitted from various combustion processes. It combines with oxygen in the atmosphere to form nitrogen dioxide (NO<sub>2</sub>), which has a characteristic brown color that should be familiar to anyone who has lived in a smoggy region. When the UV. rays of sunlight strike the NO<sub>2</sub>, it breaks off a single oxygen radical (O) that triggers many subsequent reactions of photochemical smog.



In this second reaction, we see how the single oxygen radical helps form ozone (O<sub>3</sub>). A variety of molecules can act as catalysts for this reaction.

Ozone is the single pollutant that most clearly characterizes photochemical smog. However, O<sub>3</sub>, 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<sub>2</sub> and O<sub>2</sub>:



This third reaction is called a scavenging reaction, and it happens normally in the evening.

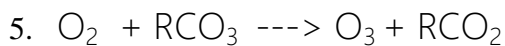
Because it converts ozone to O<sub>2</sub>, the net result is a drop in the ozone concentration in the evenings.

This is a cyclic process that needs light and nitrogen oxides to generate oxygen atoms.

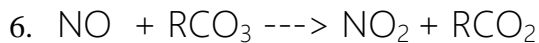


The fourth reaction shifts our attention to the hydrocarbons (represented here as RC).

When combined with the oxygen free radical, it forms RCO, which represents a variety of aldehydes and ketones. Some of these constituents can combine with oxygen to form peroxide radicals ( $\text{RCO}_3$ ).

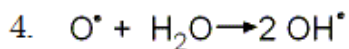


The fifth reaction demonstrates the importance of these peroxide radicals ( $\text{RCO}_3$ ) - it enhances the formation of ozone.



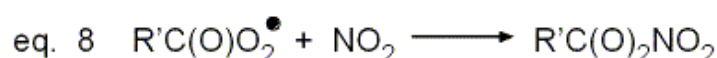
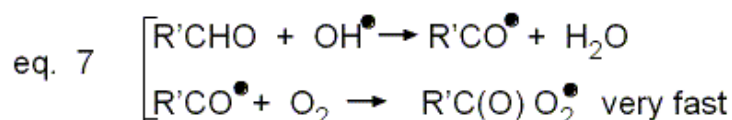
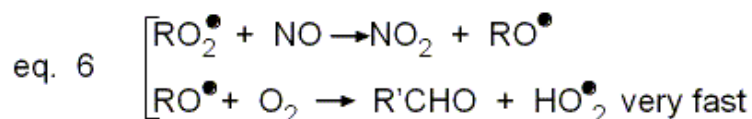
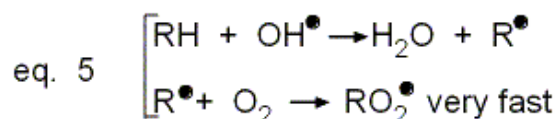
The last reaction shows a more subtle role of the peroxide radicals -- by enhancing the formation of nitrogen dioxide, we know that the nitrogen dioxide will go on to form more ozone.

#### **ALTERNATIVELY**



Once formed, the oxygen atoms react with water to form hydroxyl radicals.

The hydroxyl radicals then react with hydrocarbons according to equations 5 through 8 to form peroxyacyl nitrates (or PAN).



RH = any hydrocarbon (i.e.,  $\text{CH}_3\text{CH}_2\text{CH}_3$  or  $\text{CH}_3\text{CH}_3$ )

$\text{R}'\text{CHO}$  = an aldehyde ( $\text{R}'-\text{C} \begin{smallmatrix} \text{O} \\ // \\ \text{H} \end{smallmatrix}$ )

$\text{R}'\text{CO}^\bullet$  = an acyl radical ( $\text{R}'-\text{C} \begin{smallmatrix} \text{O} \\ // \\ \cdot \end{smallmatrix}$ )

$\text{R}'\text{C}(\text{O})\text{O}_2^\bullet$  = an acylperoxy radical ( $\text{R}'-\text{C} \begin{smallmatrix} \text{O} \\ // \\ \text{O}-\text{O}^\bullet \end{smallmatrix}$ )

$\text{R}'\text{C}(\text{O})\text{O}_2\text{NO}_2$  = an acylperoxy nitrate ( $\text{R}'-\text{C} \begin{smallmatrix} \text{O} \\ // \\ \text{O}-\text{O}-\text{NO}_2 \end{smallmatrix}$ )

When R' is a methyl group ( $\text{CH}_3-$ ) this substance is called Peroxyacetyl nitrate, or PAN

In summary, this is what happens in photochemical smog formation

1. Nitrogen oxides generate oxygen atoms
2. Oxygen atoms form hydroxyl radicals
3. Hydroxyl radicals generate hydrocarbon radicals
4. Hydrocarbon radicals form hydrocarbon peroxides
5. Hydrocarbon peroxides form aldehydes
6. Aldehydes form aldehyde peroxides
7. Aldehyde peroxides form peroxyacetyl nitrates

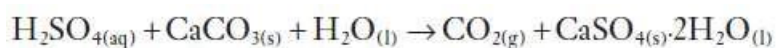
- ❖ There is no fog when Los Angeles smog forms, and visibility does not decline to just a few metres, as was typical of London fogs. Of course, the Los Angeles smog forms best on sunny days.
- ❖ London fogs are blown away by wind, but the gentle sea breezes in the Los Angeles basin can hold the pollution 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 ms <sup>−1</sup>	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 <sub>3</sub> , NO, NO <sub>2</sub> , 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 <sub>2</sub> /smoke)
Materials damaged	Rubber cracked (O <sub>3</sub> )	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  $\text{SO}_2$  and one of the first effects seems to be the inhibition of photosynthesis.
- The traditional smog generated by coal burning contained  $\text{SO}_2$  and its oxidation product,  $\text{H}_2\text{SO}_4$ . Sulphuric acid is a powerful corrosive agent and rusts iron bars and weathers building stones through the reaction:



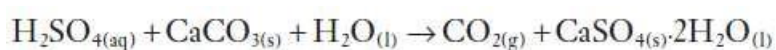
Sulphuric acid converts limestone ( $\text{CaCO}_3$ ) into gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The deterioration is severe because gypsum is soluble and dissolves in rain. Perhaps more importantly, gypsum occupies a larger volume than limestone, which adds mechanical stress so that 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  $\text{NO}_2$  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  $\text{H}_2\text{SO}_4$  on stone surfaces in those cities that have moderate  $\text{SO}_2$  concentrations.



- 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  $\text{O}_3$ . Many pigments and dyes are also attacked by  $\text{O}_3$ . 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.

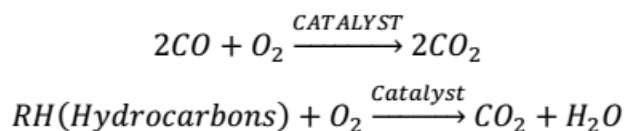
- Topography also affects a smog event. Towns located in valleys are more affected by photochemical smog because the surrounding hills and mountains reduce airflow, allowing the amounts of pollutants to rise. Valleys are also sensitive to photochemical smog because there is a stronger tendency for temperature 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*

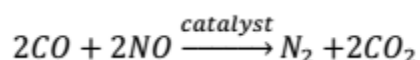
#### [1] Catalytic converters

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

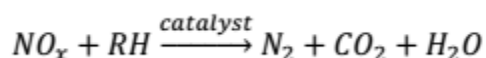
metal honeycomb bed, removes hydrocarbons and carbon monoxide from the exhaust. It is an oxidation catalyst, which converts CO to CO<sub>2</sub> and hydrocarbons to CO<sub>2</sub> and water when the exhaust gases are forced through it.



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:



NO<sub>x</sub> and hydrocarbons interact to give nitrogen, carbon dioxide and water:



## [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<sub>3</sub>, R<sub>2</sub>, RO<sub>2</sub>, H<sub>2</sub> etc.). The introduction of such compounds will slow down the conversion of NO to NO<sub>2</sub> 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

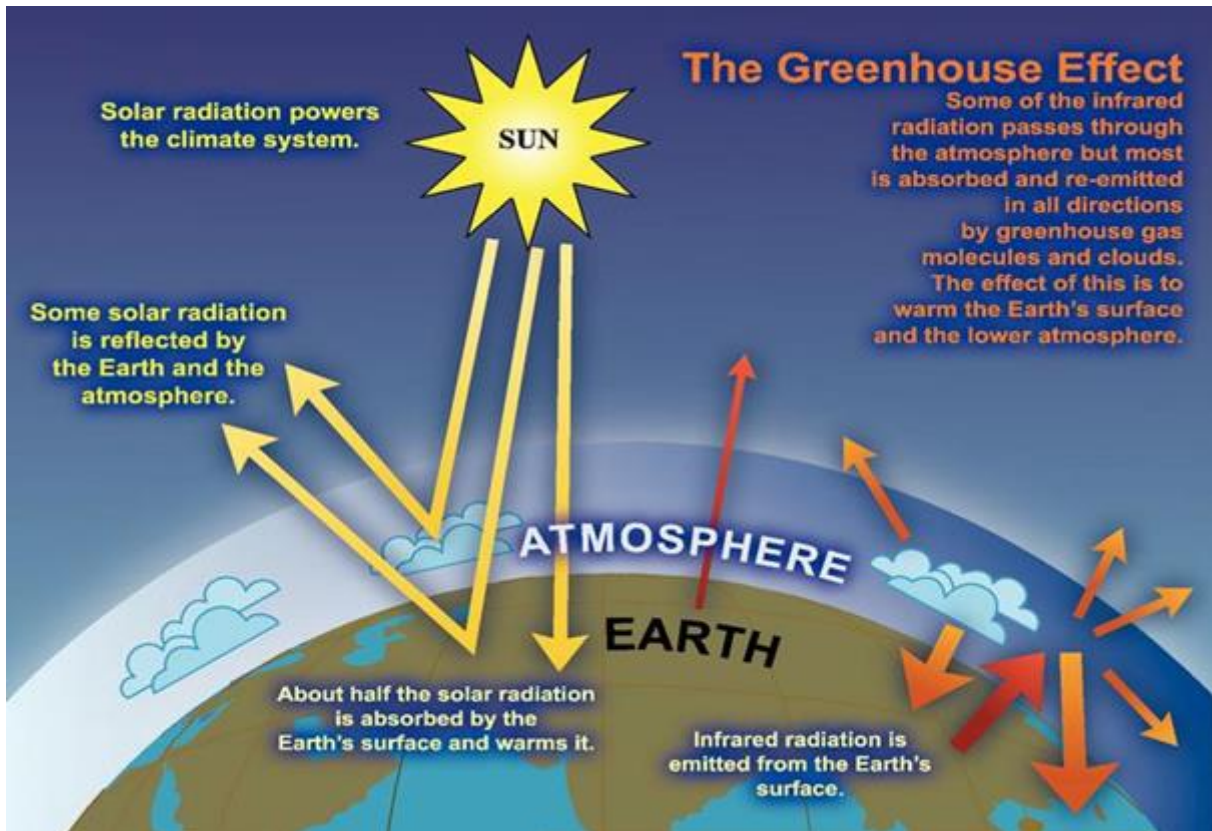
Summer petrol used in some European countries is a reformulated gasoline in which 1/10 of the aromatic hydrocarbons have been replaced by oxygenated fuel such as methyl tertiary butyl ether. These additives allow more complete and efficient combustion, thus suppressing the emission of volatile organic 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.

## GREENHOUSE EFFECT, GREENHOUSE GASES AND CLIMATE CHANGE

- ❖ The Sun powers Earth's climate, radiating energy at very short wavelengths, predominately in the visible or near-visible (e.g., ultraviolet) part of the spectrum.
- ❖ Roughly one-third of the solar energy that reaches the top of Earth's atmosphere is reflected directly back to space. The remaining two-third is absorbed by the surface and, to a lesser extent, by the atmosphere.
- ❖ To balance the absorbed incoming energy, the Earth must, on average, radiate the same amount of energy back to space. Because the Earth is much colder than the Sun, it radiates at much longer wavelengths, primarily in the infrared part of the spectrum.
- ❖ Due to greenhouse gases, the atmosphere absorbs more of this infrared energy than it reradiates to space, reradiating it back to Earth resulting in a net warming of the Earth's atmosphere system and of surface temperature. This is called the natural **greenhouse effect**.
- ❖ The Earth's greenhouse effect warms the surface of the planet. Without the natural greenhouse effect, the average temperature at Earth's surface would be below the freezing point of water approximately at  $-18^{\circ}\text{C}$ .
- ❖ However, human activities, primarily the burning of fossil fuels and of forests, have greatly intensified the natural greenhouse effect, contributing to enhanced greenhouse effect which in turn causes **global warming**.



**Greenhouse effect:** The phenomenon in which the atmosphere traps the heat coming from the sun and prevents it from escaping into the outer space.

**Global warming** refers to the recent and ongoing rise in global average temperature near Earth's surface. It is caused mostly by increasing concentrations of greenhouse gases in the atmosphere.

### Types of Greenhouse gases

Greenhouse gases comprise less than 1% of the atmosphere.

The major greenhouse gases in the atmosphere are:

- ✓ carbon dioxide ( $\text{CO}_2$ ),
- ✓ methane, ( $\text{CH}_4$ ),
- ✓ nitrous oxide ( $\text{N}_2\text{O}$ ),
- ✓ chlorofluorocarbons (CFCs) and

- ✓ ozone ( $\text{O}_3$ ).
- ✓ Atmospheric water vapour ( $\text{H}_2\text{O}$ ) also makes a large contribution to the natural greenhouse effect but it is thought that its presence is not directly affected by human activity.
- ❖ Major atmospheric gases ( $\text{N}_2$ ,  $\text{O}_2$ , Ar, etc.) do not cause greenhouse effect. These major gases make up about 99% of the atmosphere but are transparent to both incoming sunlight and outgoing infrared radiation. The actual greenhouse effect is caused by trace gases that make up less than 1% of the atmosphere, but effectively trap heat.
- ❖ The molecular structure dictates whether a gas can absorb the specific wavelengths of IR radiation necessary to trap heat and contribute to the greenhouse effect.
  - ✓ Greenhouse gases, such as carbon dioxide and water vapor, are asymmetrical molecules that absorb and re-emit IR radiation emitted by the Earth's surface. This absorption causes their molecules to vibrate and bend in specific ways, a process known as exciting a vibrational mode.
  - ✓ Symmetrical diatomic molecules ( $\text{N}_2$  and  $\text{O}_2$ ) and monatomic gases (Ar) have no net change in their electrical charge distribution (dipole moment) when they vibrate or move. Consequently, they cannot interact with the electric field of IR photons (packets of energy) and thus do not absorb thermal radiation.
- ❖ IR absorption is the process by which greenhouse gases trap heat in the atmosphere. The more IR radiation a gas absorbs, the more effectively it contributes to global warming. The number of vibrational modes relates to the complexity of the molecule

and its ability to absorb different wavelengths of IR radiation. However, methane ( $\text{CH}_4$ ) contributes less to global warming than carbon dioxide ( $\text{CO}_2$ ), despite having more IR absorption modes:

Several factors determine a gas's contribution to global warming:

- ✓ IR Absorption Spectrum: The specific wavelengths and intensities of IR radiation a gas absorbs.
- ✓ Atmospheric Concentration: The amount of the gas present in the atmosphere.
- ✓ Atmospheric Lifetime: How long the gas persists in the atmosphere before being broken down or removed.
- ✓ Global Warming Potential (GWP): A measure of how much energy the emissions of 1 ton of a gas will absorb over a given period, relative to the emissions of 1 ton of carbon dioxide ( $\text{CO}_2$ ).

*Compare  $\text{CH}_4$  and  $\text{CO}_2$*

- ✓ IR Absorption:  $\text{CH}_4$  has more modes of vibration and can absorb more IR radiation than  $\text{CO}_2$
- ✓ Atmospheric Concentration: The concentration of  $\text{CO}_2$  in the atmosphere is significantly higher than that of  $\text{CH}_4$
- ✓ Atmospheric Lifetime:  $\text{CH}_4$  has a shorter atmospheric lifetime (around 12 years) compared to  $\text{CO}_2$  (which can persist for hundreds of years).
- ✓ Global Warming Potential (GWP): While  $\text{CH}_4$  absorbs more IR radiation, its lower concentration and shorter lifetime result in a lower overall contribution to global warming compared to  $\text{CO}_2$

*Livestock influences on Greenhouse effect*

Almost all sectors within livestock production affect the atmosphere, as well as our surrounding environment. There is not only carbon dioxide that is emitted by livestock

but also methane  $\text{CH}_4$ .  $\text{N}_2\text{O}$ , nitrous oxide is also released through livestock feed production which are grown using nitrogen-based fertilizers. They are all greenhouse gases thereby contributing to greenhouse effect.  $\text{N}_2\text{O}$  molecules are more effective than  $\text{CO}_2$  in absorbing heat, and besides, they are very long-lived in the atmosphere. In addition, clearing of tropical forests and rain forests to get more grazing land causes a further increase in  $\text{CO}_2$ .

### Consequences of Enhanced Greenhouse Effect

#### i) Global Warming

- ✓ Increase of greenhouse gases concentration causes a reduction in outgoing infrared radiation, thus the Earth's climate must change somehow to restore the balance between incoming and outgoing radiation.
- ✓ This "climatic change" will include a "global warming" of the Earth's surface and the lower atmosphere as warming up is the simplest way for the climate to get rid of the extra energy.
- ✓ However, a small rise in temperature will induce many other changes, for example, as the atmosphere warms due to rising levels of greenhouse gases, its concentration of water vapor increases, further intensifying the greenhouse effect. This in turn causes more warming, which causes an additional increase in water vapor, in a self-reinforcing cycle.
- ✓ Additional important feedback mechanisms involve clouds. Clouds are effective at absorbing infrared radiation and therefore exert a large greenhouse effect, thus

warming the Earth. Clouds are also effective at reflecting away incoming solar radiation, thus cooling the Earth. A change in almost any aspect of clouds, such as their type, location, water content, cloud altitude, particle size and shape, or lifetimes, affects the degree to which clouds warm or cools the Earth.

## ii) Sea Level Rise

- ✓ If global warming takes place, sea level will rise due to two different processes. Firstly, warmer temperature cause sea level to rise due to the thermal expansion of seawater. Secondly, water from melting glaciers and the ice sheets of Greenland and the Antarctica would also add water to the ocean.

## Potential Impact on human life

### a) Economic Impact

- ✓ Over half of the human population lives within 100 kilometres of the sea. Most of this population lives in urban areas that serve as seaports. A measurable rise in sea level will have a severe economic impact on low lying coastal areas and islands, for example, increasing the beach erosion rates along coastlines, rising sea level displacing fresh groundwater for a substantial distance inland and destruction of residential and commercial establishments.

### b) Agricultural Impact

- ✓ When temperatures rise, plants grow taller in order to cool themselves off. Their stalks become taller and their leaves become narrower and grow farther apart. This makes the plant more unstable and produce less biomass.

#### c) Effects on Aquatic systems

- ✓ The loss of coastal wetlands could certainly reduce fish populations, especially shellfish. Increased salinity in estuaries could reduce the abundance of freshwater species but could increase the presence of marine species.

#### d) Effects on Hydrological Cycle

- ✓ Global precipitation is likely to increase. However, it is not known how regional rainfall patterns will change. Some regions may have more rainfall, while others may have less. Furthermore, higher temperatures would probably increase evaporation.

### Slowing Global Warming

- Cut fossil fuel use
  - Car makers could dramatically increase the fuel economy of their cars and trucks.
  - Most electric utilities still use coal to produce electricity, spewing millions of tons of carbon dioxide and other pollution into the atmosphere every year. Part of the problem could be solved by converting these plants to burn cleaner natural gas.
- Improve energy efficiency
  - Our cars and light trucks, home appliances and power plants could be made much more efficient by simply installing the best current technology.

Energy efficiency is the cleanest, safest, most economical way to begin to curb global warming.

- We could do much more to save energy in our homes and office buildings. More energy efficient lighting, heating and air-conditioning could keep millions of tons of carbon dioxide out of our air each year.

- Reduce deforestation & plant trees

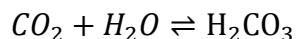
- Because global vegetation and soils contain about three times as much carbon as the planet's atmosphere, terrestrial ecosystems offer an opportunity to absorb and store (sequester) a significant amount of carbon dioxide from the atmosphere. By planting trees, preserving forests, and changing cultivation practices to increase soil carbon, for example, it is possible to increase the size of carbon sinks.

- Slow human population growth

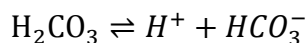
## Acid Rain

- ✓ The pH of normal rain water is 5.6 due to the dissolution of  $\text{CO}_2$  from atmosphere. When the pH of rain water drops below 5, it is called acid rain.
- ✓ Oxides of N and S are responsible for making rain water acidic
- ✓ Much of the  $\text{NO}_x$  and  $\text{SO}_x$  entering in the atmosphere are converted into  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  respectively. The detailed photochemical reactions occurring in the atmosphere are given as

Carbon dioxide in the air can dissolve in rain water to form carbonic acid,  $\text{H}_2\text{CO}_3$ .



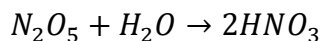
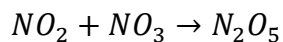
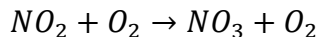
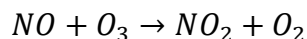
Carbonic acid is a weak acid. It partially ionises to form hydrogen ions.



The hydrogen ions from carbonic acid give natural rain water a slightly acid pH value of 5.6. Over millions of years this very dilute acidic solution has been responsible for the formation of caves in areas of limestone rocks. Limestone is made of calcium carbonate, which reacts with acids.

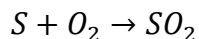


During the last century the rain water in some parts of the world has become far more acidic. This acid rain has been caused by the emission of pollutant gases such as sulfur dioxide and nitrogen dioxide.



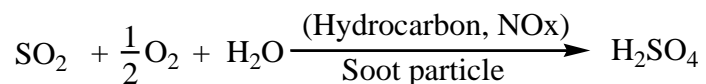
$\text{HNO}_3$  is removed as a precipitate or as particulate nitrates after reaction with bases (like  $\text{NH}_3$ , particulate lime etc).

When coal is burned in electricity power stations, sulfur impurities form sulfur dioxide.

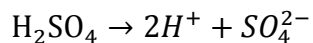


The gas is also produced when fuels obtained from crude oil are burned. When sulfur dioxide is released into the air it reacts with water and oxygen to form sulfuric acid,  $H_2SO_4$ .

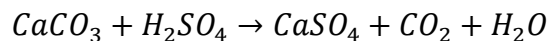
The presence of hydrocarbons and  $NO_x$  step up the oxidation rate of the reaction. Soot particles are also known to be strongly involved in catalysing the oxidation of  $SO_2$



Sulfuric acid is a strong acid. It ionises completely to hydrogen ions.



This gives rain water a pH below 5.0. Rain water that has this higher level of acidity can cause damage to buildings and statues, particularly those made of limestone. It can also reduce the growth of, or even kill, trees and crops. Acid rain may even lower pH of water in lakes, killing fish.



## Effects of Acid Deposition

- acidification of lakes and streams
  - Acid rain causes a cascade of effects that harm or kill individual fish, reduce fish population numbers, completely eliminate fish species from a waterbody, and decrease biodiversity. As acid rain flows through soils in a watershed, aluminum is released from soils into the lakes and streams located in that watershed. So, as pH in a lake or stream decreases, aluminum levels increase. Both low pH and increased aluminum levels are directly toxic to fish. In addition, low pH and increased aluminum levels cause chronic stress that may not kill individual fish, but leads to lower body weight and smaller size and makes fish less able to compete for food and habitat. Generally, the young of most species are more sensitive to environmental conditions than adults. At pH 5, most fish eggs cannot hatch. At lower pH levels, some adult fish die. Some acid lakes have no fish.
- contributes to damage of trees
  - Acid rain does not usually kill trees directly. Instead, it is more likely to weaken trees by damaging their leaves, limiting the nutrients available to them, or exposing them to toxic substances slowly released from the soil. Quite often, injury or death of trees is a result of these effects of acid rain in combination with one or more additional threats. Acidic water dissolves

the nutrients and helpful minerals in the soil and then washes them away before trees and other plants can use them to grow. At the same time, acid rain causes the release of substances that are toxic to trees and plants, such as aluminum, into the soil.

- Forests in high mountain regions often are exposed to greater amounts of acid than other forests because they tend to be surrounded by acidic clouds and fog that are more acidic than rainfall. Scientists believe that when leaves are frequently bathed in this acid fog, essential nutrients in their leaves and needles are stripped away. This loss of nutrients in their foliage makes trees more susceptible to damage by other environmental factors, particularly cold winter weather.
- accelerates the decay of building materials and paints, including irreplaceable buildings, statues, and sculptures that are part of our nation's cultural heritage.

### Controlling Acid Deposition

- Clean up smokestacks and exhaust pipes
  - Almost all electricity comes from burning fossil fuels like coal, natural gas, and oil. Acid deposition is caused by two pollutants that are released into the atmosphere, or emitted, when these fuels are burned: sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>). Coal accounts for most sulfur dioxide (SO<sub>2</sub>) emissions and a large portion of NO<sub>x</sub> emissions. Sulfur is present in

coal as an impurity, and it reacts with air when the coal is burned to form SO<sub>2</sub>. In contrast, NO<sub>x</sub> is formed when any fossil fuel is burned.

- Options for reducing SO<sub>2</sub> & NO<sub>x</sub> emissions
  - using coal containing less sulfur, washing the coal, and using devices called scrubbers to chemically remove the SO<sub>2</sub> from the gases leaving the smokestack.
  - Power plants can also switch fuels; for example burning natural gas creates much less SO<sub>2</sub> than burning coal. Certain approaches will also have additional benefits of reducing other pollutants such as mercury and carbon dioxide.
  - catalytic converters reduce NO<sub>x</sub> emissions from cars.
- Use alternative energy sources
  - There are other sources of electricity besides fossil fuels. They include: hydropower, wind energy, geothermal energy, and solar energy. There are also alternative energies available to power automobiles, including natural gas powered vehicles, battery-powered cars, fuel cells, and combinations of alternative and gasoline powered vehicles.
- Take action as individuals
  - Individuals can contribute directly by conserving energy, since energy production causes the largest portion of the acid deposition problem. For example, you can:

- Turn off lights, computers, and other appliances when you're not using them
- Use energy efficient appliances: lighting, air conditioners, heaters, refrigerators, washing machines, etc.
- Keep your thermostat at 68 F in the winter and 72 F in the summer.
- Carpool, use public transportation, or better yet, walk or bicycle whenever possible