M.Sc. Semester-III, Paper: CC-12 (Environmental Chemistry)
Unit-3 Atmosphere [By Dr. Birendra Kumar, Maharaja College]

⟹ Chemical Composition of atmosphere:

In thermosphere of the atmosphere, the temperature rises once again. Here atmospheric gases split into atoms and undergo ionisation by absorbing solar radiation.

(A) Particles, ions & radicals in the atmosphere:

Particles are the important components of the troposphere. They may vary in number from several hundred per cc depending upon the purity of air. Colloidal size particles in atmosphere are known as aerosols. These particles originate from vegetation. Other particles of natural origin in atmosphere are bacteria, fog, pollen grains and volcanic ash. They have several important effects.

* They are responsible for electrical phenomenon in atmosphere, cloud and fog formation
* They play an important role in determining the heat balance of the earth's atmosphere through light reflection.
* They serve as nuclei for the formation of ice crystals and water droplets.
* They are involved in several chemical reactions in the atmosphere:
  (i) Neutralization reactions in water droplets
  (ii) Catalytic effects of small particles of metal oxides on oxidation reactions
  (iii) Photochemical reactions of oxidation.

⟹ Formation of Inorganic Particulate Matter (Metaloxide): Metaloxides form a major group of inorganic particulates in atmosphere. They originate from the combustion of fuels. Thus, iron oxide ($Fe_3O_4$) originates by combustion of iron pyrite containing coal.

$$\underset{\text{(Iron pyrite)}}{3FeS_2} + 8O_2 \xrightarrow{\text{Combustion}} Fe_3O_4 + 6SO_2\uparrow$$

Part of $CaCO_3$ present in ash fraction of coal is converted to Calcium oxide (CaO).

$$CaCO_3 \xrightarrow[\text{(heat)}]{\Delta} CaO + CO_2\uparrow$$

Automobiles are source of lead particles in atmosphere. Leaded gasolines (Petrol, Diesel) discharge lead halides through the exhaust system.

$$\underset{\text{(Tetraethyl lead)}}{Pb(C_2H_5)_4} + O_2 + \underset{\text{Dichloroethane, Dibromoethane}}{\text{(halogenated scavengers sweet cleaner)}} \longrightarrow PbCl_2 + PbBr_2 + PbBrCl + CO_2 + H_2O$$

Aerosols mists arise from sulphuric acid obtained by oxidation of $SO_2$ which collects water vapour to form small liquid droplets.

$$2SO_2 + O_2 + 2H_2O \longrightarrow 2H_2SO_4 \text{ (Sulphuric acid)}$$

In the presence of basic air pollutants, such as $NH_3$ or CaO, salts are formed.

$$\underset{\text{(Droplet)}}{H_2SO_4} + 2\underset{\text{(Gas)}}{NH_3} \longrightarrow \underset{\text{(Droplet)}}{(NH_4)_2SO_4} \quad ; \quad \underset{\text{(Droplet)}}{H_2SO_4} + \underset{\text{(Particles)}}{CaO} \longrightarrow \underset{\text{(Droplet)}}{CaSO_4} + H_2O$$

⟹ Formation of Organic particulate Matter: It originate from a wide variety of sources: emission from vegetation and automobiles, combustion of fuels etc. Average formula of such matter is

| C | H | O | S | halogen(X) | alkoxy |
|---|---|---|---|---|---|
| (32·4) | (48) | (3·8) | (0·083) | (0·065) | (0·12) |

Polycyclic (polynuclear) aromatic hydrocarbons in Organic particulate matter are known as benzo(α-)pyrene. (  ). It commonly occurs in urban atmosphere. They originate from the pyrolysis of higher paraffins present in fuels and plant materials.

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High molecular weight paraffins are pyrolysed to yield $C_{10}H_{22}$ which undergoes further pyrolysis.

$C_{10}H_{22} \xrightarrow[-H_2]{\Delta}$  ⟶ Polycyclic aromatic hydrocarbons.

Most of polycyclic aromatic hydrocarbons (PAH) compounds absorbed on soot particles. Soot is formed as a residue on combustion of fuels in power plants and automobiles. It is highly condensed product of polynuclear aromatic hydrocarbons. In general, atmospheric particles enter human bodies through the respiratory tract which causes health hazards.

(B) The major differences between tropospheric & stratospheric air lies in the concentration of ozone, which is 10ppm in stratospheric compared to 0.05ppm in troposphere. This increased ozone concentration has a beneficial effect for life of living organism.

In stratosphere $O_3$ (ozone) is formed by photochemical reaction of $O_2$.

$O_2 \xrightarrow{h\nu} O+O$ ; $O+O+M \longrightarrow O_2+M$ ; $O_2+O+M \longrightarrow O_3+M$.

(Where M is third body like nitrogen or any other inert molecule)

Ozone ($O_3$) so formed undergo photodissociation in following manner.

$O_3 \xrightarrow{h\nu} O_2+O+heat$.

Thus, there exists a dynamic equilibrium between formation and decomposition of $O_3$ molecules. The heat generated during decomposition increases temperature of stratosphere. While photochemical process absorbs most of the harmful radiations ozone thus acts as a protective cover against UV radiations.

Mesosphere lies above the stratosphere. The ionosphere which overlaps the mesosphere extends from 50km to thousand of km. Ionic species such as $O_2^+$, $O^+$ & $NO^+$ are produced by Sun's ultraviolet radiation. The species so produced undergo ion molecule reactions as: $N_2+O^+ \longrightarrow NO^+ + N$ ; $N_2^+ + O \longrightarrow NO^+ + N$

$N_2^+ + O_2 \longrightarrow N_2 + O_2^+$ ; $NO^+ + e \longrightarrow N + O$

Oxygen ($O_2$) undergoes photolytic dissociation generating atomic oxygen.

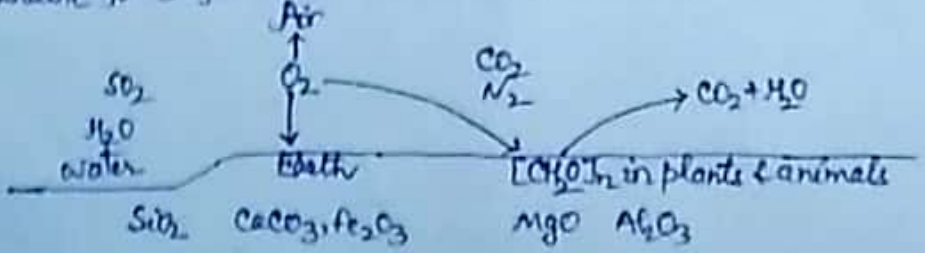
$O_2 \xrightarrow{h\nu} O+O$

⟹ Chemical and photochemical reactions in the atmosphere:

Chemicals in the atmosphere participate in photochemical reactions by absorption of solar radiation. Such reactions occur even in the absence of chemical catalysts at much lower temperature. Different chemical processes are absorbed under varying atmospheric conditions (i.e; composition, temperature, humidity and intensity of sunlight.

(i) $O_2$ & $O_3$ Chemistry: $O_2$ plays an important role in troposphere while $O_3$ in stratosphere

The stable forms of almost all the elements are oxide as shown below:

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The atmosphere contains $CO_2$ & $SO_2$ while oceans are full of $H_2O$. Earth crust mainly contains solid oxides of Si, C, Ca, Mg, Fe & Al.

In upper atmosphere the species of oxygen are $O_2, O, O^+$ & $O_3, O^*, O_2^*$, i.e, molecules, atoms ions and excited atoms and molecules. Ultraviolet radiation causes photochemical dissociation, ionisation etc.

$$O_2 \xrightarrow{h\nu} O + O \; ; \quad O_3 \xrightarrow{h\nu} O^* + O_2 \; ; \quad O \xrightarrow{h\nu} O^+ + e$$

$$O_2 \xrightarrow{h\nu} O_2^+ + e$$

Ozone ($O_3$) is the important species in the stratosphere, acting as a protective radiation shield for living organism on earth. It is formed by a photochemical reaction followed by following body reactions:

$$O_2 \xrightarrow{h\nu} O + O \; ; \quad O + O_2 + M \longrightarrow O_3 + M \; (\text{where } M = N_2 \text{ or } O_2)$$

The third body(M) absorbs the excess energy liberated by the above reaction and stabilizes the $O_3$ molecule.

Ozone strongly absorbs ultraviolet light in the region and thereby protect life on earth from severe radiation damage. Only small fraction of ultraviolet light reaches the lower atmosphere and the earth.

Mechanism of $O_3$ removal is not well understood. It is believed that ozone is eliminated by reaction with atomic oxygen, reactive $\bar{O}H$ radicals and mainly by nitric oxide.

$$O_3 + O \longrightarrow 2O_2 \; ; \quad O_3 + \bar{O}H \longrightarrow O_2 + H\bar{O}O \; ; \quad H\bar{O}O + O \longrightarrow \bar{O}H + O_2$$

$$O_3 + NO \longrightarrow NO_2 + O_2 \; ; \quad NO_2 + O \longrightarrow NO + O_2$$

It may be noted that nitric oxide is produced in the stratosphere, below 30km by the reaction of nitrous oxide ($N_2O$) with excited oxygen atoms and above 30km by ionising radiation on nitrogen.

$$N_2O + O^* \longrightarrow 2NO \; ; \quad N_2 \xrightarrow{h\nu} N + N \; ; \quad O_2 + N \longrightarrow NO + O$$

(ii) <u>$SO_2$ Chemistry</u>: There are four routes along which $SO_2$ may react:

(a) Photochemical reactions
(b) photochemical and chemical reactions in presence of nitrogen oxide.
(c) Chemical process in water droplets containing metal salts & $NH_3$.
(d) Reactions on solid particles in the atmosphere.

$SO_2$ absorbs solar radiation in lower atmosphere to produce electronically excited state of $SO_2^*$.

$$SO_2 + h\nu \longrightarrow SO_2^*.$$

In natural sunlight, the overall reaction is

$$SO_2 + \tfrac{1}{2}O_2 + H_2O \longrightarrow H_2SO_4$$

The free radical $\bar{O}H$ present in photochemical smog also contributes to the oxidation of $SO_2$, ending up as a sulphate.

$$H\bar{O} + SO_2 \longrightarrow HOS\bar{O}_2 \; ; \quad HOS\bar{O}_2 + O_2 \longrightarrow HOSO_2 + O_2^- \; ; \quad HOSO_2O_2^- + NO \longrightarrow HOSO_2\bar{O} + NO_2$$

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In relatively humid atmospheres, $SO_2$ is oxidised by reactions occurring inside water droplets, which proceed faster in presence of $NH_3$ and catalyst.

$$NH_3 + SO_2 + H_2O \longrightarrow NH_4^+ + HSO_3^-$$

$$NH_3 + HSO_3^- \longrightarrow NH_4^+ + SO_3^{2-}$$

$SO_2$ one of the air pollutant is responsible for smog, resulting in several incidents of loss of human life. It also contributes to acid rains.

(iii) Nitrogen Oxide ($NO_x$) Chemistry: the nitrogen oxides ($NO_x$) in the atmosphere are nitrous oxide ($N_2O$), nitric oxide ($NO$) and nitrogen dioxide ($NO_2$).

Nitrous oxide ($N_2O$) originates from microbiological processes and occurs in unpolluted air. In the lower atmosphere it has no influences on chemical reactions, but at higher altitudes, it helps deplete the ozone layer.

$$N_2O \xrightarrow{h\nu} N_2 + O \; ; \quad N_2O + O \longrightarrow NO + NO$$

$$NO + O_3 \longrightarrow NO_2 + O_2.$$

Nitric oxide and nitrogen dioxide are important constituents of polluted air. These oxides ($NO$, $NO_2$) enter the atmosphere by combustion of fossil fuels. Bulk of $NO_x$ originates from bacterial decay of organic matter in the earth's surface, which yields $N_2O$. This reacts with oxygen atom to form $NO$ & then enters the $O_3$ destruction cycle. This cycle is disrupted when $NO_2$ reacts with $OH$ (radical) to give $HNO_3$.

At the next step $NO$ reacts with $OH$ to produce $HNO_2$ (nitrous acid). This acid, being soluble in water, is quickly rained out.

The overall process for the elimination of $NO$ probably consists of its reaction with $O_2$, $O_3$ to yield $NO_2$.

$$2NO + O_2 \longrightarrow 2NO_2 \; ; \quad NO + O_3 \longrightarrow NO_2 + O_2 \; ; \quad NO + O \longrightarrow NO_2$$

The photo dissociation of $NO_2$ can yield a series of inorganic reactions and finally ends up as $HNO_3$, nitrates or organic nitrogen compounds.

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO \; ; \quad N_2O_5 + H_2O \longrightarrow 2HNO_3$$

Nitric acid ($HNO_3$) produced from $NO_2$ is removed as acid rains.

An additional factor regarding man-made ($NO_x$) load in stratosphere may be taken into account. Nuclear explosions produce large quantity of $NO_x$ which are injected directly into the stratosphere. This will lead to extensive reduction in the $O_3$ shield.

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