M.Sc. III Semester

Paper- III

Section- A

ENVIRONMENTAL CHEMISTRY

Atmosphere (Unit-II)

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CHEMICAL COMPOSITION OF ATMOSPHERE: PARTICLES, IONS&RADICALS IN THE ATMOSPHERE.

PARTICLES: Particles are the Important contents of the troposphere. They may vary in the number from several hundred/cc in very pure air to more than 10^5/cc in highly polluted air. Their size is in the range of 0.1 μ to 10μ. The particulate mass level ranges from 10μg/m^3 in clean air to 60-2000μg/m^3 in polluted air in urban areas.

Colloidal size particles in atmosphere are known as aerosols. Aerosols of natural origin having diameters <0.2μ are known as Aitkin Particles. Small solid particles and liquid droplets are collectively called particulates. The various particles existing in nature include dust, mist, smoke, fog, pollen grains, bacteria and volcanic ash. Inorganic particulates such as FeO, CaO, etc may result from combustion of coal and metallurgical operations. Organic particulates arise from automobile exhausts and combustion of fuels etc.

Particles in the size range of 0.1μ to 1.0μ manifest several important effects in the atmosphere-

1. They are responsible for electrical phenomena in the atmosphere, cloud and fog formation
2. They play an important role in determining the heat balance of the earth's atmosphere through light reflection.
3. They serve as nuclei for the formation of ice crystals and water droplets through the condensation of water vapour.
4. They absorb and destroy free radicals thereby reducing the rate of free radical chain reactions.

5. They are involved in several chemical reactions in the atmosphere such as neutralization reactions and photochemical oxidation reactions involving dust and aerosols.
6. The absorption of gases on some solid surfaces may change the absorption spectrum of the gas for sun light such as O_2 absorbed on carbon particles might absorb sun light more strongly than free oxygen atoms.

Chemical processes for formation of inorganic particulate matter:

Metal oxides form a major group of inorganic particulates in atmosphere

$3FeS_2 + 8O_2 \rightarrow Fe_3O_4 + 6SO_2$

They originate from combustions of fuels thus the particulate iron oxide originates in combustion of pyrite containing coal.

$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$

Part of the calcium carbonate in ash fraction of coal is converted to calcium oxide and discharged through the stack.

Automobiles are sources of lead particles in the atmosphere. Combustion of leaded gasoline discharged lead halides through exhaust system.

$Pb(C_2H_5)_4 + O_2 + (\text{halogenated scavengers})$

$\rightarrow PbCl_2 + PbBr_2 + PbBrCl + CO_2 + H_2O$

Aerosol mists arise from sulfuric acid, obtained by oxidation of sulphur dioxide which collects water vapour to form small liquid droplets.

$2SO_2 + O_3 + 2H_2O \rightarrow 2H_2SO_4$

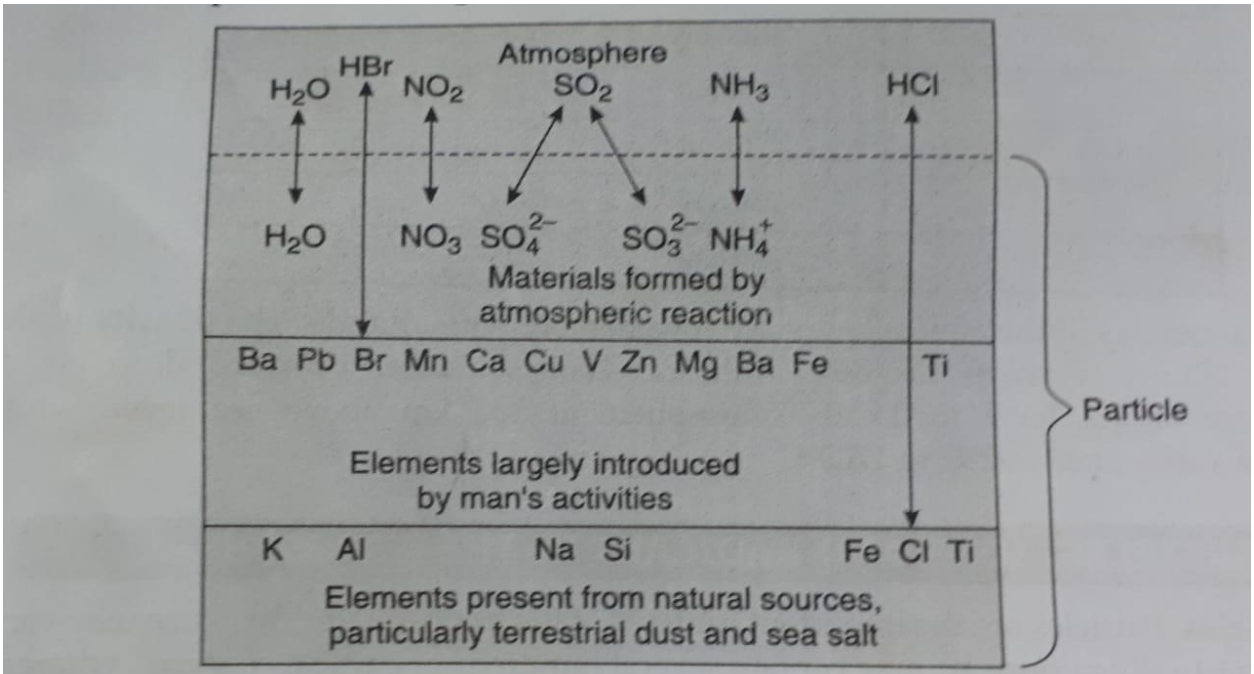
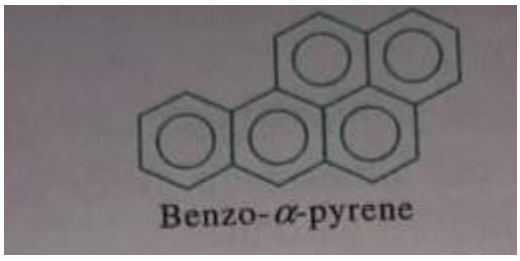


Fig. 1. The components and origins of inorganic particulate matter.

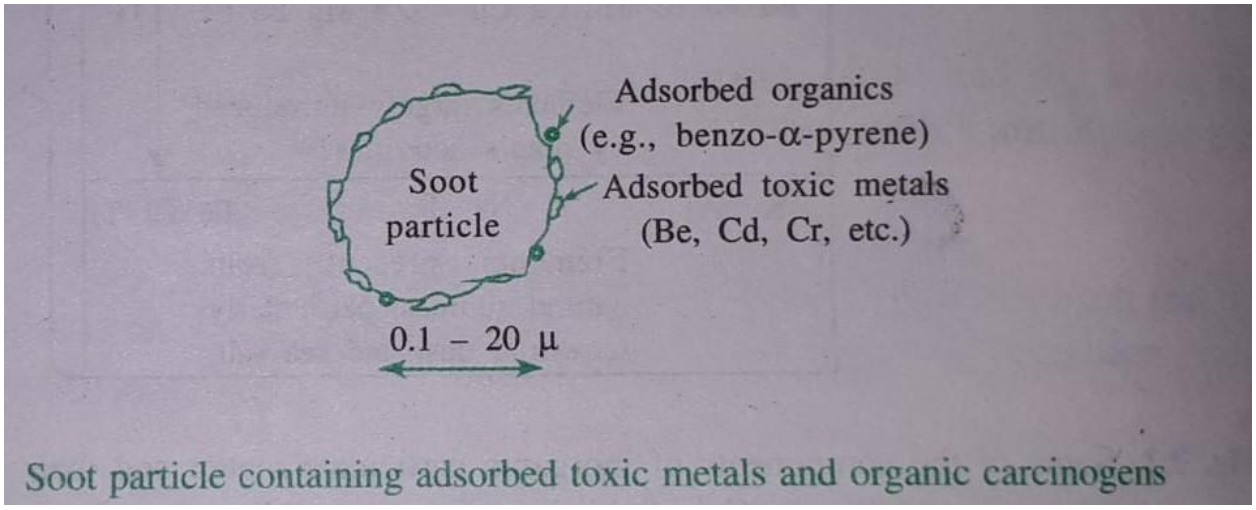
Chemical processes for formation of organic particulate matter:

Organic particulate matter originates from a wide variety of sources e.g. emission from vegetation and automobile, combustion of fuel, etc. Polycyclic or polynuclear aromatic hydrocarbons in organic particulate matter are known to have carcinogenic effect e.g. benzo-α-pyrene.



They originate from pyrolysis of higher paraffins present in fuels and plant materials. High molecular weight paraffines are pyrolyzed to yield $C_{10}H_{22}$ which undergoes further pyrolysis

Most of the polycyclic aromatic hydrocarbons remain adsorbed on soot particle. (Soot is formed as residue on combustion of fuel in power plants and automobiles)



Soot particle containing adsorbed toxic metals and organic carcinogens

It accounts for 55% of particulates load in in urban areas. It is highly condensed product of polynuclear aromatic hydrocarbons, consisting of several thousand interconnected crystallites i.e., graphic platelets each having about hundred condensed aromatic rings. The H-content of soot is 1-3% and O-content 5-10% due to partial surface oxidation. Because of its large surface area, soot acts as a carrier of toxic organics such as benzo-α-pyrene and toxic trace metals such as Be, Cd, Cr, Mn, Ni, V etc.

In general, atmospheric particles enter human bodies through the respiratory tract. Among these, small particles of 0.1-1.0μ size reach the lungs and are retained there, causing health hazards. Removal of particulate matter from gas streams is an important strategy for air pollution control.

IONS: U.V. radiation is primarily responsible for the production of ions in ionosphere. At night in absence of U.V. radiation, the +ve ions slowly recombine with free electrons to form the original neutral species. This process occurs rapidly in lower regions of the ionospheres where the species exist relatively in high concentration.

The ions are strongly influenced by the earth magnetic field, giving rise to the phenomenon of Van Allen Belts. This consists of two belts of ionizing particles encircling the earth.

The ions dominate above stratosphere in region known as ionosphere. Both +ve ions such as O_2^+, O^+, NO^+ and electrons exist at significant levels in ionosphere. They persist for long periods without recombining to give neutral species due to rarefied conditions in the upper atmosphere.

RADICALS: Besides ions, free radicals are generated by electromagnetic radiations. They consist of atoms or group of atoms with unpaired electrons having half lives of several mins in the rarefied upper atmosphere. They are highly reactive, they take part in chain reactions in which one of the products of each reaction is a free radical. Finally, one of the free radicals in chain is destroyed and the chain is terminated.