Gaseous Atmospheric Chemical species

- **Inorganic oxides**: CO, CO_2, SO_2, NO_2
- **Oxidants**: O_2, O_3, H_2O_2, $HO\cdot$, $HO_2\cdot$, organic $RO_2\cdot$ radicals, NO_3
- **Reductants**: CO, SO_2, H_2S
- **Organics** also reductants: CH_4, alkanes, alkenes & aryl compounds
- **Oxidized organic species**: carbonyl, organic nitrates
- **Photochemically active species**: NO_2, HCHO, acids (H_2SO_4), bases (NH_3), salts (NH_4HSO_4)

Unstable Reactive species NO_2^*, $HO\cdot$

Aerosols

Clouds

Chemical and Photochemical Reactions in the Atmosphere:

1. Oxygen and O_3 Chemistry:

$$O_2 + h\nu \xrightarrow{135\text{-}136\,nm} O + O$$

$$O_3 + h\nu \xrightarrow{308} O\cdot + O_2$$

$$O + h\nu \longrightarrow O^+ + e^-$$

$$O_2 + h\nu \longrightarrow O_2^+ + e^-$$

→ O_3 is formed by photochemical R_x^n.

$$O_2 + h\nu \xrightarrow{242\,nm} O + O$$

$$O + O_2 + M\ (N_2 \text{ or } O_2) \longrightarrow O_3 + M$$

Role of third body (M) to absorb the excess energy thereby stabilize O_3 molecule.

Role of O_3: Absorption of UV light in the region 220-230 nm and thereby protects life on earth from severe radiati damage.

Mechanism of O_3 Removal:

O_3 is eliminated by R_x^n with

- Atomic oxygen: $O_3 + O \rightarrow O_2 + O_2$
- HO·: $O_3 + HO\cdot \rightarrow O_2 + HOO\cdot$; $HOO\cdot + O \rightarrow HO\cdot + O_2$
- NO: $O_3 + NO \rightarrow NO_2 + O_2$; $NO_2 + O \rightarrow NO + O$

→ Nitric oxide is produced in the stratosphere below 30 km by the reaction of nitrous oxide (N_2O) with excited oxygen atoms above 30 km by ionizing radiation on nitrogen.

$$N_2O + O\cdot \longrightarrow 2NO$$
$$N_2 + h\nu \longrightarrow N + N$$
$$O_2 + N \longrightarrow NO + O$$

Reaction of SO_2

1. Photochemical Reactions
   $SO_2 + h\nu$ (300-400 nm) → SO_2^* (lower atm)
2. Photochemical and chemical R_x^n in the presence of NO_x & / or hydrocarbons
3. Chemical processes in water droplets containing metal salts and NH_3
4. R_x^n on sol particles the atmosp

2. Photochemical and Chemical Reaction in the Presence of NO_x and/or Hydrocarbons:

$$SO_2 + \frac{1}{2}O_2 + H_2O \xrightarrow{R\cdot H\cdot = 32\text{-}90\%} H_2SO_4$$

natural (5-30 ppm)

sunlight This reaction is promoted by the presence of hydrocarbons and NO_x.

$$HO\cdot + SO_2 \longrightarrow HOSO_2\cdot$$

from photochemical smog

$$HOSO_2\cdot + O_2 \longrightarrow HOSO_2O_2\cdot$$
$$HOSO_2O_2\cdot + NO \longrightarrow HOSO_2O\cdot + NO_2$$

3. Chemical Processes in water droplets containing metal salts and NH_3:

$$NH_3 + SO_2 + H_2O \xrightarrow[Ni(II),\ Cu(II)\ etc.]{\text{Catalyst } Mn(II),\ Fe(II)} NH_4^+ + HSO_3^-$$

Inside water aerosol droplets

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

4. Reaction on solid Particles in the atmosphere:

Rxn on soot particle.

Heterogeneous oxidation of SO_2

→ SO_2 is responsible for smog.

Reaction of Nitrogen Oxides

NO_x

N_2O — NO ← Imp. constituent of polluted air → NO_2

Nitrous oxide originates from microbiological processes and occurs in unpolluted air at a level of about 0.25 ppm. In lower atmosphere, it has practically no influence on chemical Rx; but at higher altitudes, it helps to deplete the ozone layer.

$N_2O + h\nu \longrightarrow N_2 + O$

$N_2O + O \longrightarrow NO + NO$

$NO + O_3 \longrightarrow NO_2 + O_2$

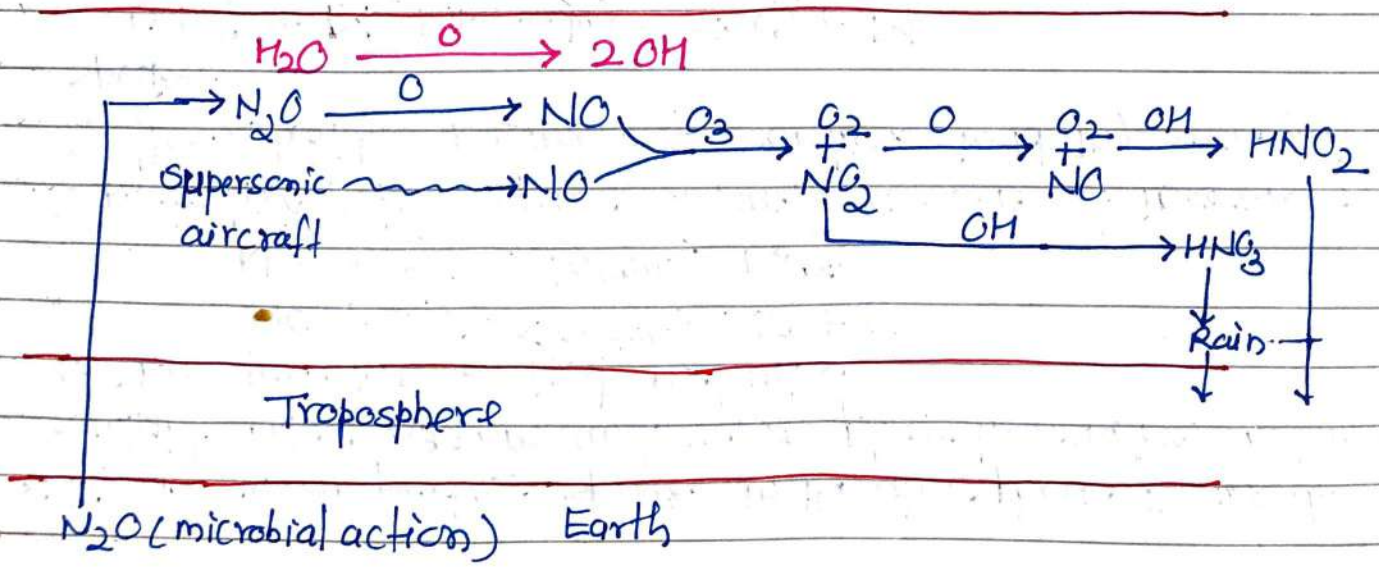
Sources and sinks for NO_x: The bulk of NO_x on a global basis originates from microbial action in the earth's surface, which yields N_2O. This N_2O is inert in the troposphere but it reacts with O atom in the stratosphere to form NO and then enters the O_3 destruction cycle. This cycle is disrupted when NO_2 reacts with OH· to give HNO_3.

→ At the next step NO reacts with OH· to produce HNO_2. These acid being water soluble in H_2O, are quickly rained out in the troposphere.

$2NO + O_2 \longrightarrow 2NO_2$

$NO + O_3 \longrightarrow NO_2 + O_2$

$NO + O + M$ (third body) $\longrightarrow NO_2 + M$



→ NO_2 is an important species in the atmosphere. It absorbs sunlight below 398 nm undergoing photodissociation and above 430 nm forming excited molecules.

$$NO_2 + h\nu \xrightarrow{<398nm} NO + O$$

$$NO_2 + h\nu \xrightarrow{>430nm} NO_2^*$$

→ The photodisociation of NO_2 can yield a series of inorganic reactions, besides a number of reactions involving organic species.

$$O + O_2 + M(\text{third body}) \longrightarrow O_3 + M$$

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

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$

$$O + NO_2 \longrightarrow NO + O_2$$

$$O + NO_2 + M \longrightarrow NO_3 + M$$

$$NO_2 + NO_3 \longrightarrow N_2O_5$$

$$NO + NO_3 \longrightarrow 2NO_2$$

$$O + NO + M \longrightarrow NO_2 + M$$

→ NO_2 finally ends up as HNO_3, NO_3^- or organic nitrogen compounds

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

In stratosphere, NO_2 also reacts with HO· to form HNO_3

$$NO_2 + HO\cdot \longrightarrow HNO_3$$

→ NO_2 also reacts with bases (NH_3, particulate lime) to yield particulate nitrates.

Chlorofluorocarbons (CFC): Apart from Nox, chlorine also plays an effective role in removing O_3 in the stratosphere.

$$Cl\cdot + O_3 \longrightarrow Cl{-}O\cdot + O_2$$
$$Cl{-}O\cdot + O \longrightarrow Cl\cdot + O_2$$
$$Cl{-}O + NO_2 \longrightarrow Cl{-}O{-}N(=O)=O$$

Sources and sinks for Cl

Sources

CFC

Aerosol spray

$$CFCl_3 \xrightarrow{h\nu} CFCl_2 + Cl\cdot$$
$$Cl\cdot + O_3 \longrightarrow ClO\cdot + O_2$$
$$ClO\cdot + O \longrightarrow Cl\cdot + O_2$$

Sinks:

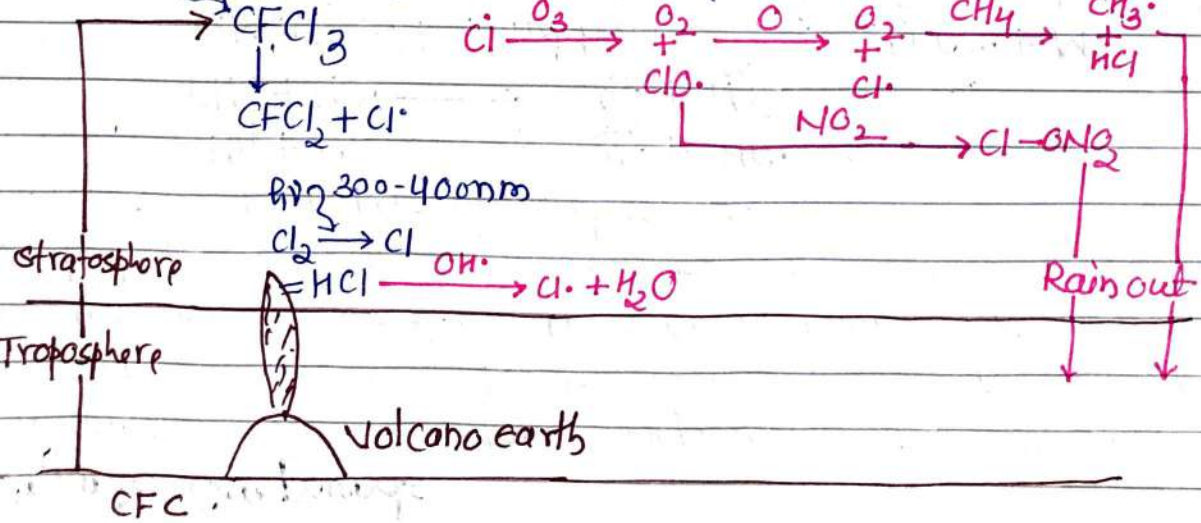
$$Cl + O_3 \longrightarrow ClO\cdot + O_2$$
$$ClO\cdot + O \longrightarrow Cl\cdot + O_2$$
$$Cl\cdot + CH_4 \longrightarrow CH_3\cdot + HCl$$
$$ClO\cdot + NO_2 \longrightarrow ClONO_2$$

] rained out

Volcanoes inject Cl_2 and HCl

$$Cl_2 \xrightarrow[\text{stratosphere}]{h\nu} 2Cl\cdot$$

$$HCl + OH\cdot \longrightarrow Cl\cdot + H_2O$$



Organic Compounds

→ Hydrocarbons and other organic compounds in the atmosphere are susceptible to oxidation through a series of steps of chemical and photochemical reactions. As a result many noxious secondary pollutant products and intermediates are produced, which belong to the category of photochemical smog.

$$CH_4 + O_2 \longrightarrow CH_3\cdot + HO\cdot$$
$$CH_4 + HO\cdot \longrightarrow CH_3\cdot + H_2O$$
$$CH_3\cdot + O_2 + M \text{ (third body)} \longrightarrow CH_3COO\cdot + M$$

→ Organic compounds in the atmosphere readily enter into reactions with O_3, NO_3 and free radicals such as $HOO\cdot + HO\cdot$ etc.

$$HO\cdot + CH_2{-}CH{=}CH_2 \longrightarrow CH_2{-}\dot{C}H{-}CH_2OH$$

Free radicals are generated from photochemical reactions as well as chemical reactions.

$$CH_3CHO + h\nu \longrightarrow CH_3\cdot + HCO\cdot$$
$$C_3H_7OO\cdot \longrightarrow CH_3COCH_3 + HO\cdot$$