INTERACTIVE PROCESSES IN THE ATMOSPHERIC ENVIRONMENT

A.P. MITRA

Council of Scientific & Industrial Research
Rafi Marg, New Delhi 110 001, INDIA

Interactive chemical processes are discussed for different levels of our extended atmospheric environment for which the upper boundary has now been pushed to the far reaches of the earth-sun space. Four specific regions are involved. These are:

(i) The *tropospheric* level dominated by the chemistry of greenhouse gases of biospheric, volcanic or anthropogenic origin;

(ii) The *stratospheric* level dominated by the ozone problem and marked by an increasing role of solar radiation;

(iii) The *ionospheric* level with high power R.F. heating and injections ·(inadvertent or deliberate) of active gases modifying the ionosphere; and

(iv) The *plasmasphere* level allowing precipitation of trapped particles from powerline perturbations.

In this paper, the canvas will be this total environment, but the discussions will be limited to (i), (ii) and (iii).

Atmospheric chemistry for each region as we go from the troposphere through the stratosphere to the mesosphere and the ionosphere with specific identification of the natural and anthropogenic sources is described in some detail. In the first two regions the reactions are primarily neutral; in the mesosphere and ionosphere primarily ionic. There are specific boundaries where the nature of the chemistry changes.

Problems relating to quantitative estimations of budgets, identification of sources and sinks, life history of the source gases and specific benchmarks (e.g. Antarctic ozone hole, lagapedo and HAEO-C ionospheric hole experiments) are examined.

HISTORICAL BACKGROUND

Atmospheric chemistry—both neutral and ionic—has held the centre stage of atmospheric studies for more than three decades since IGY when rocket and satellite

sensors discovered unexpectedly high concentrations of NO and NO^+ (both photochemical products) over a large portion of the middle and upper atmospheres and of hydrated complex positive and negative ions in the lower ionosphere. Ozone was already known as a major photochemical product. It became increasingly clear that minor constituents, existing in small abundances (a few parts per billion to a few parts per million) play a surprisingly dominant role over the entire atmospheric environment. Since the concentrations are small, these can be substantially altered through relatively small inputs, some of which, we now realize, come from industrial and agricultural practices and are, therefore, man-made.

Since these early periods of IGY and IQSY, atmospheric chemistry has moved from one region of the earth's atmosphere to another, and from the earth's atmosphere to the atmospheres of the planets with the exciting observations of Mariner IV which flew past Mars in 1964 and the discoveries of ionospheres and magnetospheres in several planets. The very intense research efforts on the terrestrial atmosphere and ionosphere in the 50's and 60's provided a backdrop for new studies of the planetary atmospheres and ionospheres as results from Venus and Mars began to come in. Reactions tried out in the earth's ionosphere were applied to the planetary atmospheres under different conditions of temperature and pressure and different neutral environment. In other words, studies of the ionospheres of the earth and the planets became complementary.

As the attention of atmospheric chemists moved to the earth's stratosphere and the troposphere with the warning on possible ozone destruction by CFM's in the early seventies and more recently on climatic roles of CO_2-NO_x-CFM-CH_4-O_3-H_2O system, the examples of runaway greenhouse effect adding about 500 K in Venus where CO_2 environment is 70,000 times larger than on earth and the cold Mars with little CO_2 in its atmosphere began to be used as benchmarks. It was apparent that the present optimum greenhouse warming of about +30K will not remain so in future. It is interesting to trace the sequence of changes in the interest of atmospheric chemists over the last three decades. This is shown in Fig.1. The very intensive interest in the anomalies of ion composition of the earth's ionosphere shifted partially to the planetary ionospheres and then in the seventies to the stratosphere and now to the troposphere as new results began to emerge on the role and effects of non-CO_2 greenhouse molecules.

SOME KEY ELEMENTS

An important element is that different levels of the earth's atmospheric environment are not isolated and that effects of human activities are not limited to the troposphere-stratosphere system but extend to ionosphere and magnetosphere. One must, therefore, consider the earth's entire environment as one entity. The upper boundary of this environment has with time been pushed upwards to the far reaches of the earth-sun space to the end of the tail swept out by the solar wind. The earth, in this context, behaves just like a comet. We are thus concerned with physical and
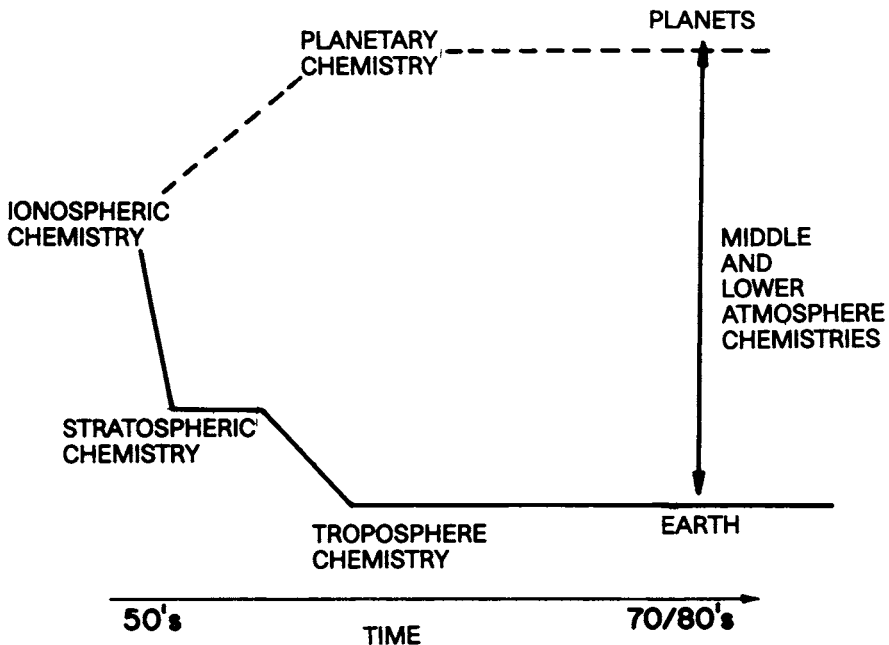
Fig. 1. A historical perspective of atmospheric chemistry research.

chemical processes of a vast region several earth radii in extent, coupled through flow of energy and matter, with chemical reactions acting as a filter.

In Fig. 2 we reproduce (from a SCOSTEP document) the linkage and interaction between the sun and this extended atmospheric environment comprising the magnetosphere, the ionosphere, the middle atmosphere and the lower atmosphere. The sun and the radiation and particles it hurls into space are at the centre of this interaction with variable radiations in the ultraviolet and X-rays and with a number of periodicities from the widely recognized 11 and 22 years to the Milancovitch cycle.

There are several key boundaries in the atmospheric environment which demarcate regions of substantially different chemistries. These boundaries are different for chemistries involving neutral particles and for ions. But for both some basic boundaries can be identified. These are:

(i) The *tropopause* separates regions of local and global dynamics: below this level there is chemical filtering of source gases and also a "rainout" of molecules of short lifetime. It also separates the levels of ozone chemistry (stratosphere) from those of greenhouse molecules (troposphere);

(ii) The *stratopause* dividing the predominantly neutral chemistry below to a mixture of neutral and ion chemistry and the beginning of the ionosphere (~60km);
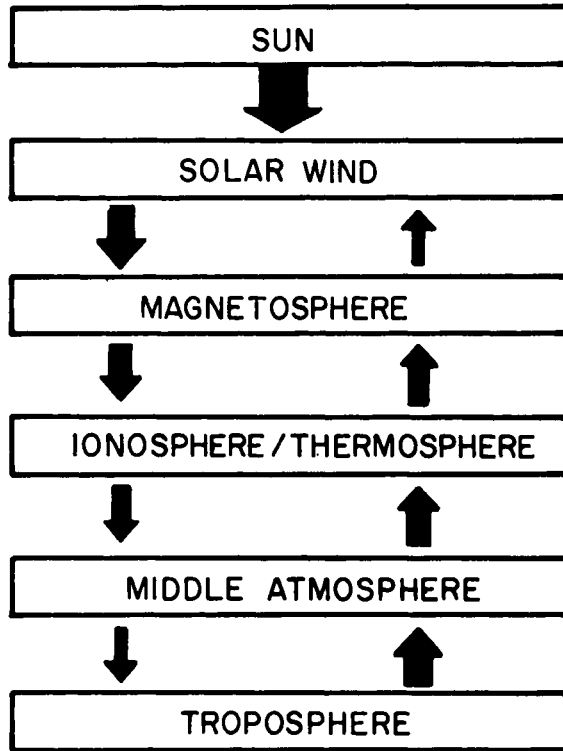
Fig. 2. Energy transfer mechanism.

(iii) The *mesopause*, the coldest region in the atmospheric environment, at which temperature, concentration of atomic oxygen and ionic recombination show drastic changes; this is also the boundary where cluster ions change into simple molecular ions;

(iv) Levels 110-120km: above these levels diffusive separation of neutral particles begins resulting in increasing predominance of lighter particles (particularly O, H, and He) with increasing altitude; and

(v) Levels around 180km: these levels separate the region of molecular ions (below) from the region of atomic ions (above).

A simplified picture classifying these regions and the different boundaries is shown in Fig. 3.

Another important key question concerns the nature, magnitude and origin of sources and sinks of active species in all these regions. The mesopause provides a
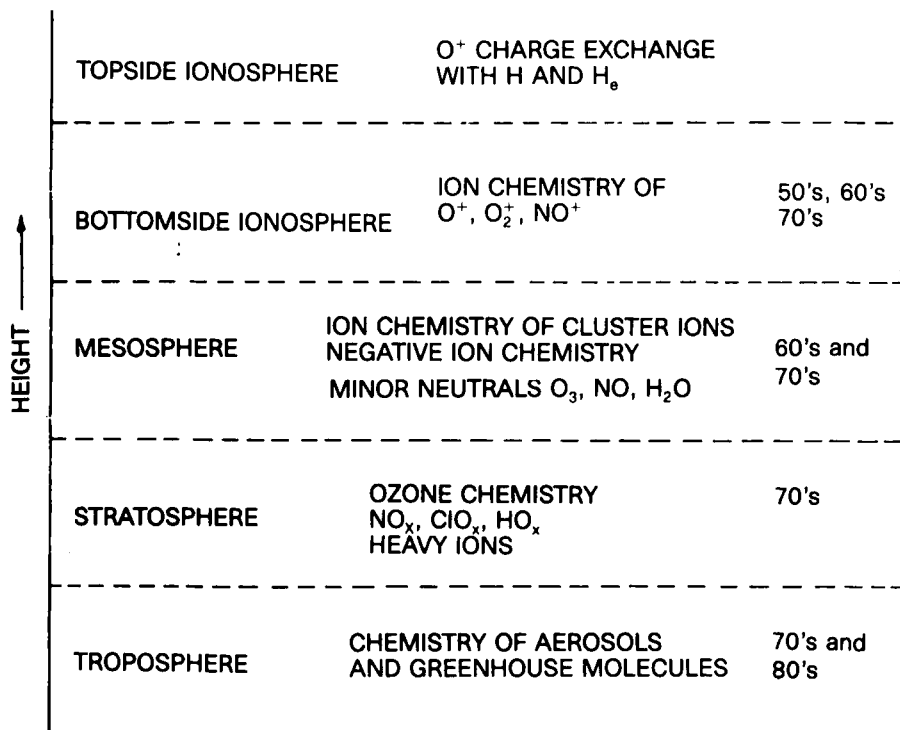
HEIGHT ↑	TOPSIDE IONOSPHERE	O^+ CHARGE EXCHANGE WITH H AND H_e	
	BOTTOMSIDE IONOSPHERE	ION CHEMISTRY OF O^+, O_2^+, NO^+	50's, 60's 70's
	MESOSPHERE	ION CHEMISTRY OF CLUSTER IONS NEGATIVE ION CHEMISTRY MINOR NEUTRALS O_3, NO, H_2O	60's and 70's
	STRATOSPHERE	OZONE CHEMISTRY NO_x, ClO_x, HO_x HEAVY IONS	70's
	TROPOSPHERE	CHEMISTRY OF AEROSOLS AND GREENHOUSE MOLECULES	70's and 80's

Fig. 3. Diagrammatic representation of different chemical regions.

rough boundary below which the active species are predominantly terrestrial in origin, and above which predominantly extra-terrestrial.

The interactive chemical picture of the atmospheric environment presented in this address covers this extended canvas. For brevity only a few dominant aspects are discussed. The connecting thread is the role of human activities. At least four levels (Fig. 4) are involved where effects of human activities are discernible: for two of these the effects are approaching those from natural sources. These levels are:

(i) The *troposphere-stratosphere* system dominated by ozone chemistry and CO_2-CH_4-H_2O-N_2O-CFM greenhouse molecules;

(ii) The *ionospheric level* modified (inadvertently or deliberately) by (a) highpower high-frequency transmissions and (b) injections of active gases from rocket exhausts or as tracers; and

(iii) The *plasmasphere and magnetosphere level*, normally a reservoir of trapped solar particles, precipitating some of these particles as a result of large powerline perturbations.

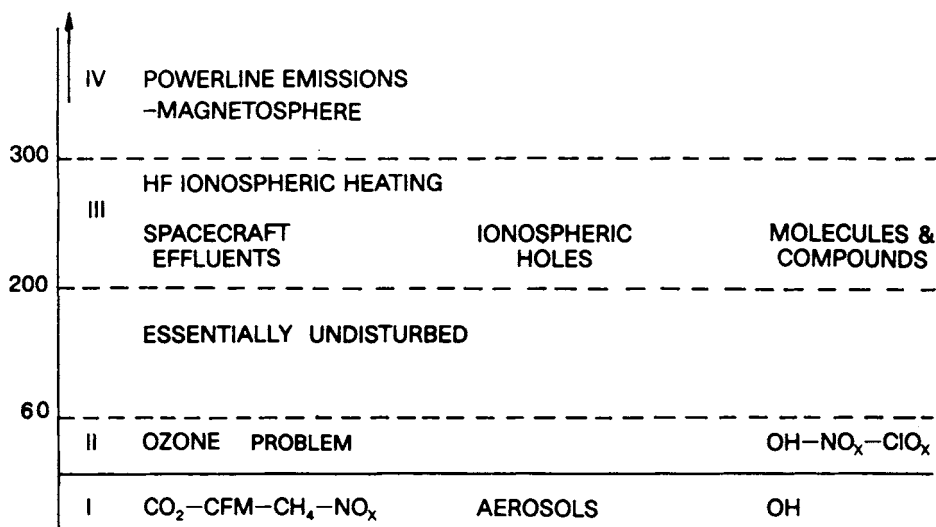In this presentation we will limit ourselves to (i) and (ii) only.

IV	POWERLINE EMISSIONS –MAGNETOSPHERE		
III	HF IONOSPHERIC HEATING		
	SPACECRAFT EFFLUENTS	IONOSPHERIC HOLES	MOLECULES & COMPOUNDS
	ESSENTIALLY UNDISTURBED		
II	OZONE PROBLEM		$OH-NO_x-ClO_x$
I	$CO_2-CFM-CH_4-NO_x$	AEROSOLS	OH

Fig. 4. Different levels of atmospheric environment subject to perturbation due to human activities.

CHEMISTRY OF THE EARTH'S ENVIRONMENT

Neutral chemistry

We first take up the problem of neutral chemistry. The dominant chemical reactions and the ways these change with altitudes and for different regions are shown in Fig. 5. The nature of the fluxes and their transports are shown in Fig. 6.

Troposphere is an oxidising region. The injections of active gases are of several types of origin: (i) biospheric; (ii) industrial; (iii) volcanic; and (iv) solar. At these levels only wavelengths longer than about 300nm can penetrate and hence direct dissociation of CFM or most of the greenhouse molecules does not occur. The only major exception is the photolysis of O_3 by radiations of ≤ 310 nm which produces $O(^1D)$. This process is crucial because $O(^1D)$ generates the catalytic radical OH from H_2O through the reaction $H_2O + O(^1D) \rightarrow 2OH$. Concentration of OH depends on the concentration of H_2O (highly variable) and also on the tropospheric concentration of O_3. Reaction with OH determines the lifetime of many important gases in the troposphere including the greenhouse molecules, and acts as a "chemical filter" for transport to the stratosphere. OH radicals are a major sink for CO and CH_4. An additional source of OH is HO_2 reaction with NO and O_3, and so reactions leading to HO_2 formation adds to OH production. Examples are:
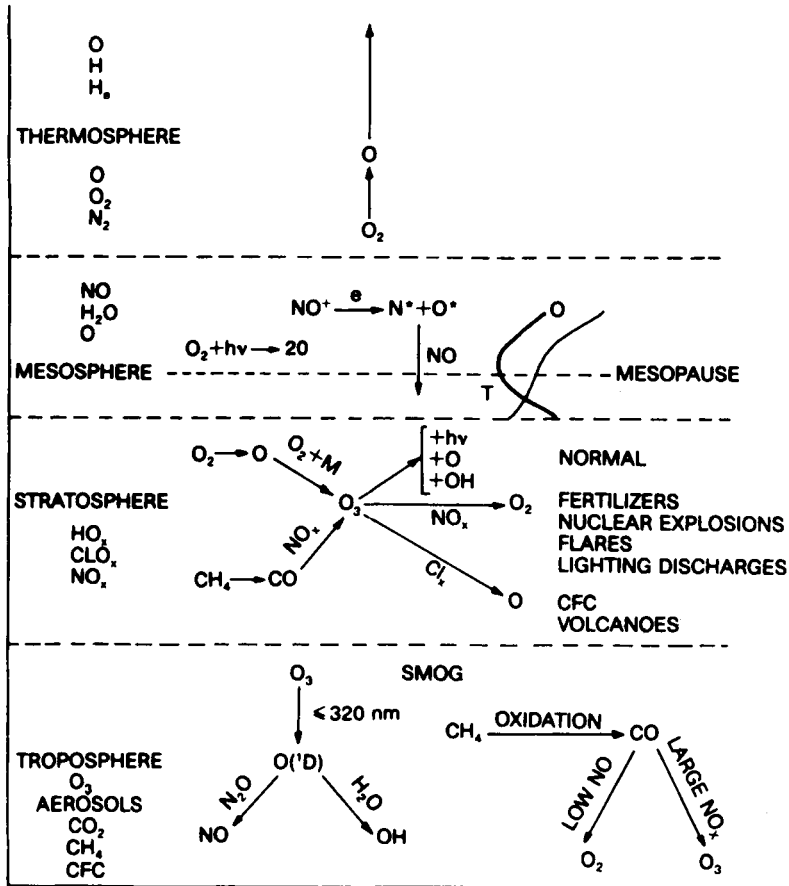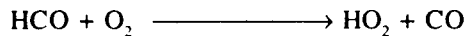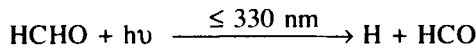
O
H
H$_o$

THERMOSPHERE

O
O$_2$
N$_2$

O

O$_2$

NO
H$_2$O
O

$NO^+ \xrightarrow{e} N^* + O^*$

$O_2 + h\nu \rightarrow 20$

NO

MESOSPHERE - MESOPAUSE

T

O

$O_2 \rightarrow O$ $O_2 + M$

$\begin{bmatrix} +h\nu \\ +O \\ +OH \end{bmatrix}$ NORMAL

STRATOSPHERE

HO$_x$
ClO$_x$
NO$_x$

O$_3$ $\xrightarrow{NO_x}$ O$_2$ FERTILIZERS
NUCLEAR EXPLOSIONS
FLARES
LIGHTING DISCHARGES

NO*

$CH_4 \rightarrow CO$

Cl*

O   CFC
VOLCANOES

O$_3$ SMOG

< 320 nm

CH$_4$ $\xrightarrow{\text{OXIDATION}}$ CO

TROPOSPHERE
O$_3$
AEROSOLS
CO$_2$
CH$_4$
CFC

O(^{1}D)

N$_2$O

NO

H$_2$O

OH

LOW NO

LARGE NO$_x$

O$_2$ O$_3$

Fig. 5. Neutral chemistry.

$$HCHO + h\nu \xrightarrow{\leq 330 \text{ nm}} H + HCO$$

$$HCO + O_2 \longrightarrow HO_2 + CO$$

$$H + O_2 + M \longrightarrow HO_2 + M$$

Thus oxidation of CH$_4$ amplifies primary OH production caused by photolysis of O$_3$. A simplified picture is shown as Fig. 7. Another special feature is that more than in stratosphere, heterogeneous chemical reactions are more often encountered here, such as in scavenging of trace gases by aerosols, clouds and precipitation.

The other main series of reactions involves CH$_4$. Oxidation of CH$_4$ can end up with O$_2$ or O$_3$ depending on the concentrations of NO If NO mixing ratio is less
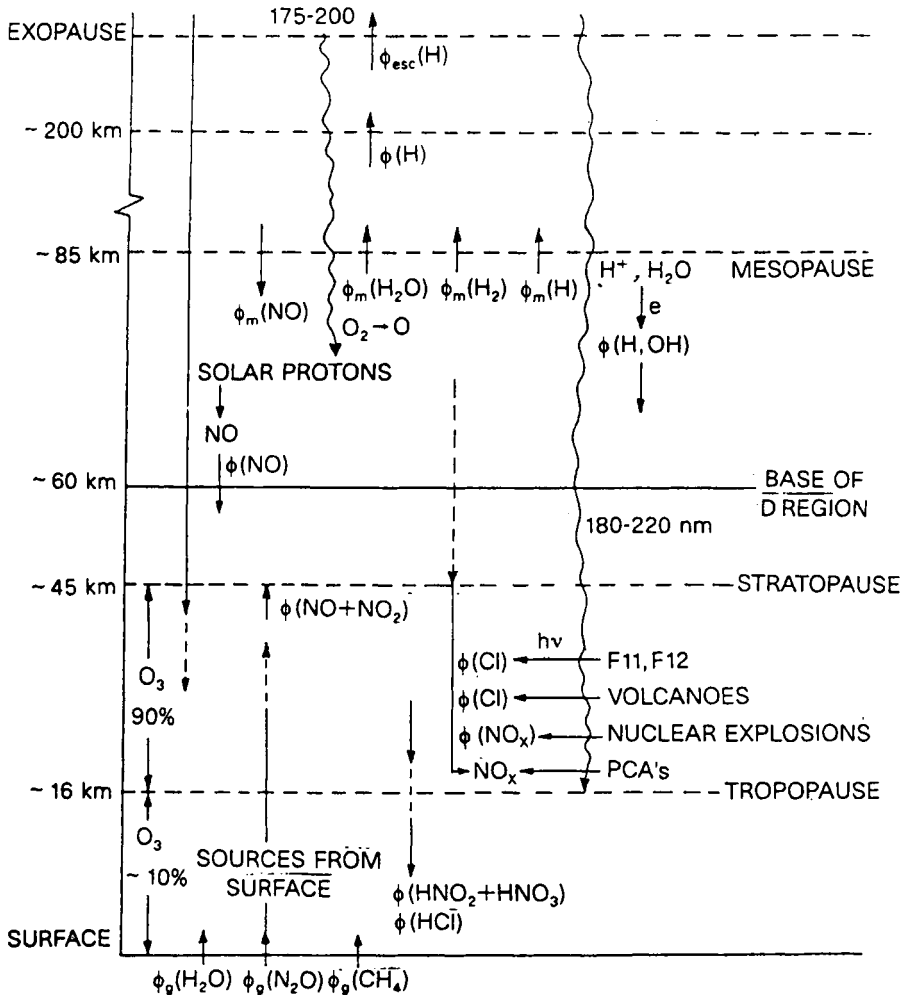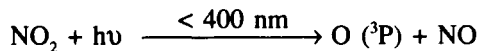
Fig. 6. Nature and sources of fluxes.

than a few pptv, then we have removal of odd oxygen (O_3) and odd hydrogen (OH, HO_2), but in polluted regions with high NO concentrations ($\geq$ a few pptv), reactions involving CH_4, CO and NO produces ozone and odd hydrogen. Thus localised production of ozone with local climatic effect can occur.

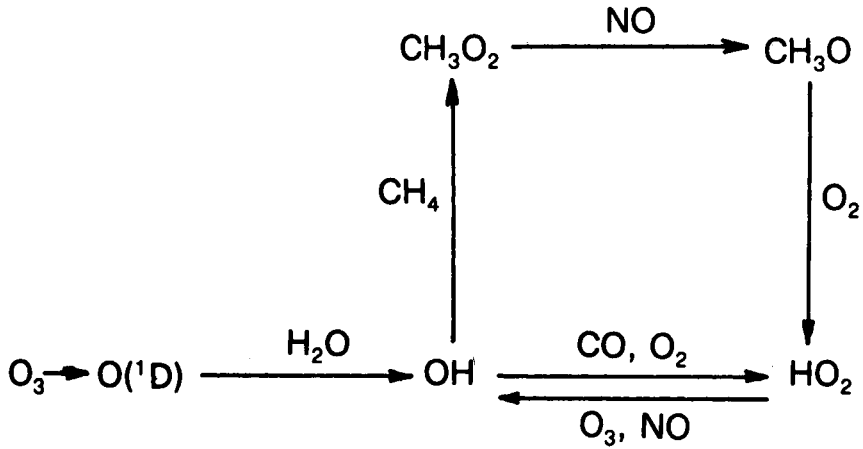The tropospheric ozone is either produced *in situ* through dissociation of NO_2 in the visible (Fig. 8).

$$NO_2 + h\upsilon \xrightarrow{\;< 400\ nm\;} O\ (^3P) + NO$$

$$CH_3O_2 \xrightarrow{\quad NO \quad} CH_3O$$

$$O_3 \rightarrow O(^1D) \xrightarrow{\quad H_2O \quad} OH \underset{O_3, NO}{\overset{CO, O_2}{\rightleftharpoons}} HO_2$$

with CH_4 connecting OH to CH_3O_2, and O_2 connecting CH_3O to HO_2.
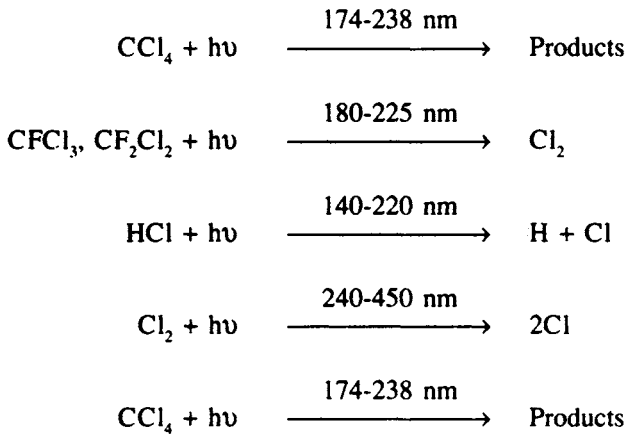
Fig. 7. Amplification of OH production.

TROPOSPHERE
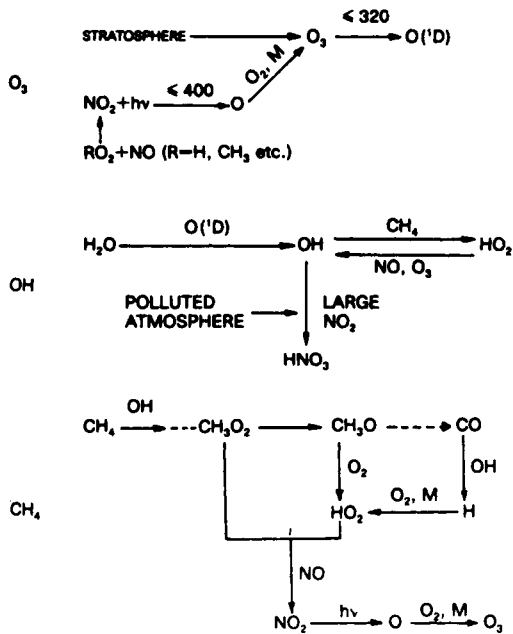
Fig. 8. Key reactions in troposphere.

followed by $O + O_2 + M \longrightarrow O_3$ reaction, or by transport from the stratosphere.

As we go into the stratosphere, several new aspects arise: firstly, solar radiations of appropriate wavelengths are now available not only for formation and destruction of ozone, but also for dissociation of CFM, CH_4, CCl_4, N_2O, H_2O and others releasing ozone-destroying active species ClO, OH and NO. The radiation involved are indicated below:

$$O_2 + h\upsilon \xrightarrow[\text{Schumann-Runge bands}]{\text{175-200 nm}} O(^3D) + O(^1D) \quad \text{Mesosphere and upper stratosphere}$$

$$O_2 + h\upsilon \xrightarrow[\text{Herzberg continue}]{\text{200-242 nm}} O + O \quad \text{Stratosphere, weakly in mesosphere}$$

$$O_3 + h\upsilon \xrightarrow[\text{Hartley band}]{\text{242-310 nm}} O_2 + O(^1D) \quad \text{Stratosphere— formation of } O(^1D)$$

$$O_3 + h\upsilon \xrightarrow[\text{Huggins band}]{\text{310-400 nm}} O_2 + O(^3D) \quad \text{Stratosphere and troposphere— formation of } O(^1D)$$

$$O_3 + h\upsilon \xrightarrow{\text{400-850 nm}} O_2 + O \quad \text{Troposphere— photodissociation even at surface}$$

$$H_2O + h\upsilon \xrightarrow{\text{135-200 nm}} OH + H$$

$$H_2O_2 + h\upsilon \xrightarrow{\text{135-370 nm}} OH + OH$$

$$NO_2 + h\upsilon \xrightarrow{\text{245-398 nm}} NO + O$$

$$\xrightarrow{\text{135-245 nm}} NO + O(^1D)$$

$$ClO + h\upsilon \xrightarrow{} Cl + O$$

$$ClO\,NO_2 + h\upsilon \xrightarrow{\text{195-450 nm}} \text{Products}$$

$$CCl_4 + h\upsilon \xrightarrow{\text{174-238 nm}} \text{Products}$$

$$CFCl_3, CF_2Cl_2 + h\upsilon \xrightarrow{\text{180-225 nm}} Cl_2$$

$$HCl + h\upsilon \xrightarrow{\text{140-220 nm}} H + Cl$$

$$Cl_2 + h\upsilon \xrightarrow{\text{240-450 nm}} 2Cl$$

$$CCl_4 + h\upsilon \xrightarrow{\text{174-238 nm}} \text{Products}$$

The depth of penetration at different wavelengths (attenuation of e^{-1} for an overhead sun) is shown in Fig. 9. The variabilities of the radiations with solar activity become important in this context (see, p. 16 under **Sources and sinks**). It may be noted that the ozone-destroying processes of anthropogenic origin come mainly through NO and ClO. These have to compete with natural sources: solar proton events for NO and volcanic eruptions for ClO.
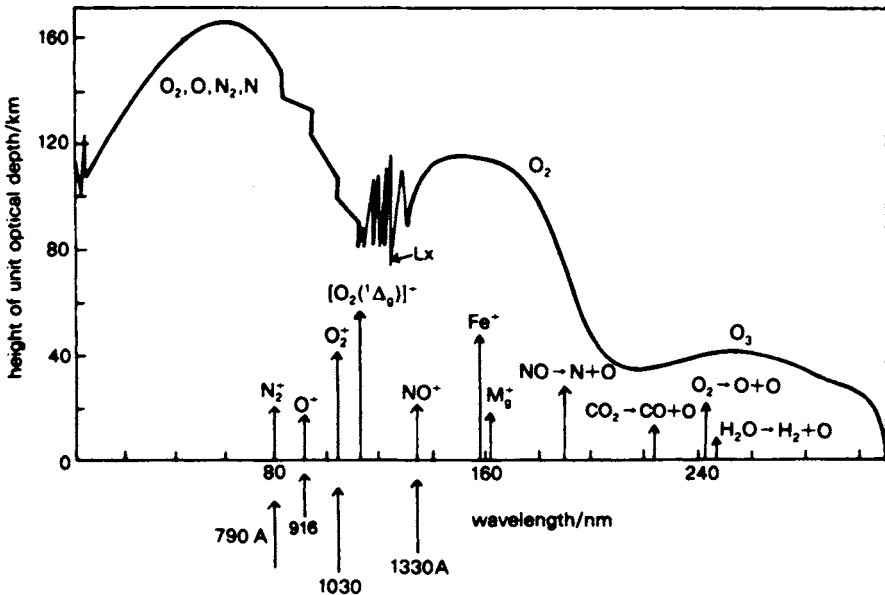
Fig. 9. Penetration of radiation to e^{-1} of intensity.

An important aspect is the oxidation of methane. The pathways of oxidation are shown in Fig. 10.

As we go to the mesosphere there is a drastic change. We are now entering the ionosphere beginning, under normal conditions, at around 60 km. Upto around 90 km where major dissociation of O_2 begins, the atmosphere remains mixed with N_2 and O_2 as major constituents. Above 90 km with dissociation of O_2 there is a rapid shifting from O_2, N_2 combination to O_2, O, N_2, N combination and at higher levels of the thermosphere to O, N combination, and then on to hydrogen and helium.

An important neutral constituent in the mesosphere, which is a minor species and a photochemical product, is NO. Its importance comes from the fact that at the lowest part of the ionosphere (60-80km) it is the main source of ionization through the process:

$$NO + h\upsilon \quad \xrightarrow{\text{Lx}} \quad NO^+ + e$$
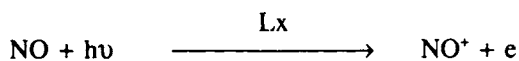
Direct formation of NO through

$$N + O + M \quad \longrightarrow \quad NO + M$$

or $\quad N + O_2, O_3 \quad \longrightarrow \quad NO + O, O_2$
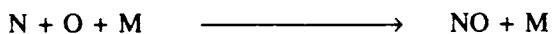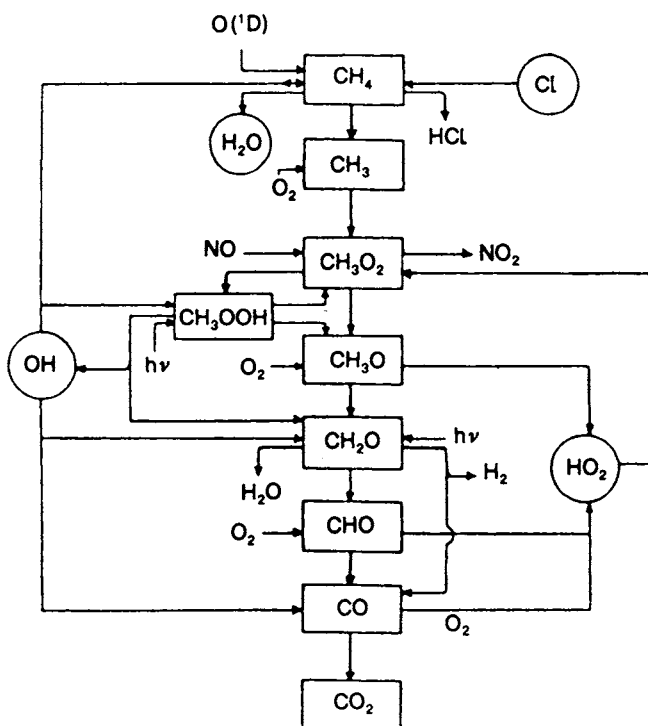
Fig. 10. Stratospheric methane chemistry (after WMO, 1985).

require the presence of atomic nitrogen but an unusual contribution comes from an ionic process:

$$NO^+ + e \longrightarrow NO + h\upsilon$$
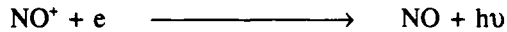
which occur in the lower part of the thermosphere; NO thus produced is transported downwards. This is one of the few processes in the atmosphere we know where a sizeable contribution to the neutral constituent is coming from an ionic process.

Ion chemistry

Although the ionosphere begins only around 60 km, the so-called "non-ionized" region of the troposphere and stratosphere also contains ions, excepting that there are no free electrons. Thus over the entire atmospheric environment we are concerned with reactions of neutrals with ions, but since neutrals are more numerous (even for minor species), these have in most cases no effect on the concentrations of the neutral species.

The key boundaries are here ~35 km, 60 km, mesopause and heights around 170-180 km.

Principal ionic reactions are summarised in Fig. 11.

The boundary around 35 km separates proton hydrates (PH) from non-proton hydrates (NPH). In the region below this level, ions become increasingly complex as we go towards the surface. The troposphere is dominated by ions of the type NH_4^+ $[(NH_3)_2SO_2]_x(H_2O)_w(NH_3)_n$ where x, w and n can take different values. The ions are heavy, additional increments in mass numbers apparently go in multiples of 98. In the stratosphere below 35 km, the positive ions are of the type $H^+(X)_n(H_2O)_n$ with X believed to be CH_3CN and negative ions $R\text{-}(HR)_m(HNO_3)_n$ with HR = 98 ± 2 AMU (observed). Ion concentrations are around $10^3 cm^{-3}$ at stratospheric heights progressively increasing from low to high latitudes. This happens because the ionizing source is galactic cosmic rays whose entry into the atmosphere is modulated by the earth's magnetic field.

It is believed that PH to NPH conversion occurs through the following reaction:

$$H^+(H_2O)_n + X \xrightarrow{\quad k \quad} H^+X(H_2O)_{n-m} + m\ H_2O$$
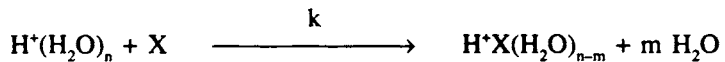
One can derive threshold concentrations of X from:

$$k[PH^+][X] = X_i\ N^-[NPH^+]$$

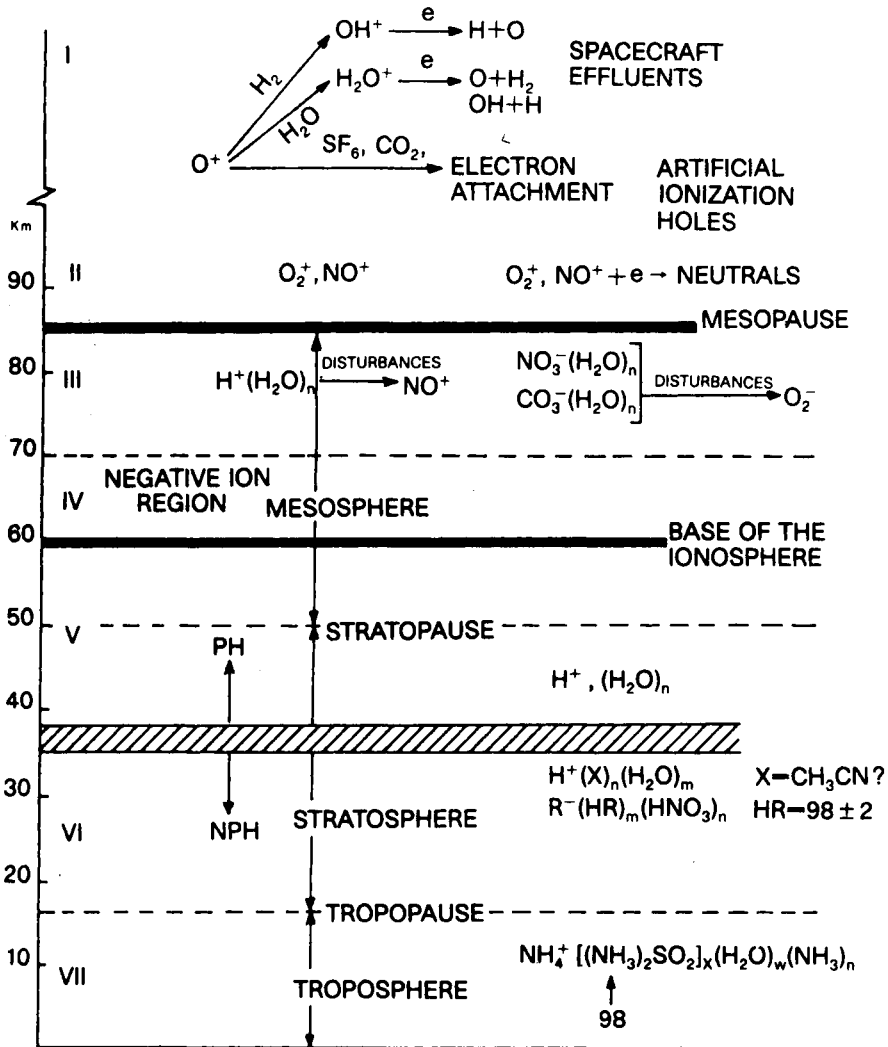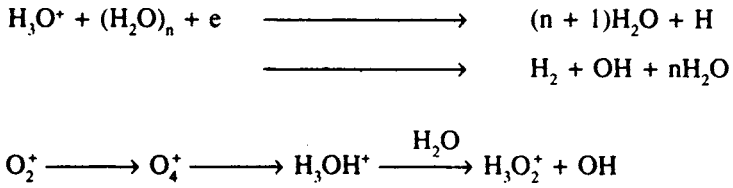This gives, at 35 km,

$$[X] \sim 10^5 cm^{-3}$$

Fig. 11. Ion chemistry.

Thus, once the *nature* of X is identified, the ionic measurement provides an estimate of the participating minor species at concentration levels well below existing measurement techniques.

In the context of anthropogenic effects, the main question is whether any of the ionic processes produce active species that could interact with ozone or any of the other greenhouse molecules.

Production of H/OH can occur through dissociative reactions:

$$H_3O^+ + (H_2O)_n + e \longrightarrow (n + 1)H_2O + H$$
$$\longrightarrow H_2 + OH + nH_2O$$

$$O_2^+ \longrightarrow O_4^+ \longrightarrow H_3OH^+ \xrightarrow{H_2O} H_3O_2^+ + OH$$

Combining the two,

Ionic production of H/OH $\leq 2q$

Actual calculations show these are negligible in the stratosphere, but can be important in mesosphere during PCA (Polar Cap Absorption) events.

Can any ionic process directly contribute to the destruction of ozone? Suggestions in the past point out the following reactions,

$$NO_3^- + O_3 \longrightarrow NO_2^- + 2O_2 + 0.8 \text{ ev} \quad (< 2 \times 10^{-12})$$
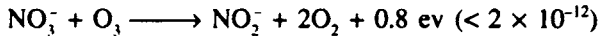
The loss rate is, however, low:

The only process, through the ionic chain, that can be of concern (especially during proton events) is given in Fig. 12.

It is important to note that a single proton event can inject NO_x into the stratosphere of a magnitude considerably larger than the GCR (Galactic Cosmic Radiation) inputs for a whole year. Thus:

	NO_x input (molecules)	
GCR	Per year	S. min 7×10^{32}
SPE	August 72	32×10^{32}

(Sudden Proton Event)

From the stratosphere to the mesosphere the main change is that we are now entering the iononsphere. At heights below 75 km, negative ions are dominant. Ions below the mesopause are of the form $H^+ (H_2O)_n$ (positive ions) and $NO_3^-(H_2O)_n$ and $CO_3^- (H_2O)_n$ (negative ions). During solar disturbance events these are reduced to the simple ions O_2^-. For man-made events, these reactions can assume importance if large amount of H_2O molecules are injected (as with rocket exhausts). Above the mesopause the cluster ions disappear and the Ionosphere is dominated principally by two molecular ions O_2^+ and NO^+ upto the next key boundary of around 170-180 km. The most important reactions are:

$$O_2^+ + e \longrightarrow O^1 + O$$
$$O_2^+, N_2^+ \longrightarrow NO^+ + e \longrightarrow N + O$$

PROTON EVENTS

SECONDARY ELECTRONS
(10-100 eV)

N_2

N_2^- N^+ N
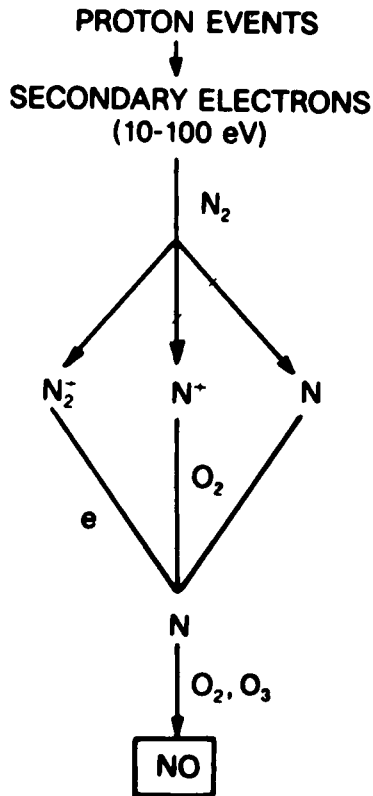
O_2

e

N

O_2, O_3

NO
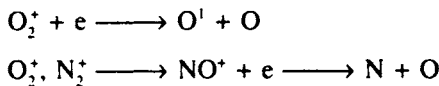
Fig. 12. NO production from solar proton events.

In this region, the predominant control is through solar radiations and no large scale effects are anticipated from man-made events.

A major difference occurs above about 170-180 km, where ions are primarily atomic: O^+. Here any injection of neutral molecules could convert O^+ ions to molecular ions with a consequent increase in recombination coefficient by as much as three orders of magnitude. This causes large scale depletion of ionization at those heights.

Sources and sinks

Solar sources — The principal sources are:

(i) Changes in solar constant;

(ii) Solar activity changes in the XUV region; and

(iii) Solar Proton Events and their occurrence frequency as a function of solar activity.

Since magnitude of variations of radiation flux with solar activity *decreases* with increase in wavelength and also since absorption coefficients of these radiations also generally decrease with increasing wavelength, sensitivity to solar activity decreases as we go down in height.

TABLE 1: Solar Flux: Wavelengths of Interest with Descending Heights

Extreme UV	10-100 nm	100-300 km	× 10	Hours to weeks to years
Lx	121.6 nm	80	× 2	Solar Cycle
UV	150		16%	Solar Cycle
	200		10%	Solar Cycle
	250		4%	Solar Cycle
	300	Surface	1%	Solar Cycle
S	$S_o = 1373 \pm 20$ Wm^{-2}			
	$\Delta S_o = 0.07 \Delta R_{m, max}$ Wm^{-2}			

Three types of changes can occur:

(i) Modulation of D-region conductivity and consequent modulation of global electrodynamics (relevant to sun-weather relationship);

(ii) Changes in ozone content and ozone profiles; and

(iii) NO production through SPEs.

For the first, we are concerned with GCR for tropospheric-stratospheric systems (*increases* with *decreasing* solar activity) and Lx (increases by 100% from sunspot minimum to maximum). For the second, at the wavelengths of interest the observed solar cycle variations are 1 to 10%. For solar proton events, NO_x injection is irregular, depending on the occurrence, magnitude and nature of the SPE. The main point to consider here is that because of the timescales involved we have to consider not just a single SPE event but the cumulative effect of such events. A rough estimate (Mitra, 1981) indicates that NO_x injection from SPEs can be roughly represented by a curve similar to that of F 10.7cm.

The solar cycle variation in the ozone profile due to such variations in the relevant radiation are comparable to those caused by increased trace gases. An example of the change from 1979 to 1986 from these two types of changes are shown in Fig. 13.

Volcanic sources

We will limit ourselves, in this discussion, to Cl_x only. An approximate way of estimating Cl_x injection from this source, is to start with Lamb's VDI/E_{max} index as a measure of the total amount of ash injected for any given eruption and then
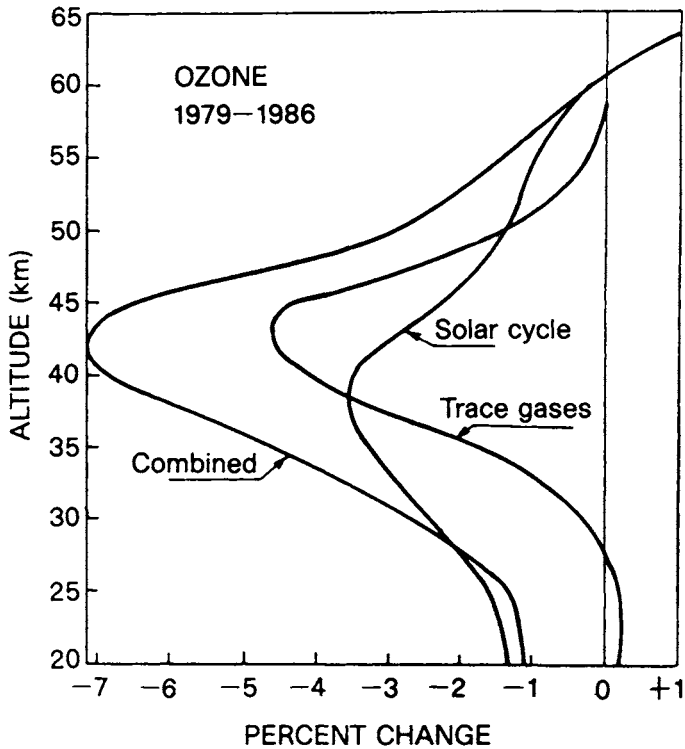
Fig. 13. Relative ozone changes between 1979 and 1986 from changes in solar radiation and those in trace species (Brasseur *et al.*, 1988).

calculate Cl_x injection by estimating $f(Cl_x) = 0.01$ $f(gas)$. This is probably an underestimate as the observations for Mt Agung eruption of 1963 showed. An appropriate basis would be:

$$0.1 \ f \ (gas) > f(Cl_x) > 0.01 \ f \ (gas).$$

Representative values are shown below:

Cl_x injection for moderate volcano ~ 10^{34} molecules
Mt Agung 3×10^{32}

Volcanoes inject not only Cl_x but also a number of other species of greenhouse interest. For Mount St. Helens eruption, the reported estimates were:

CO_2 (ppmv)	< 3-19
H_2 (ppmv)	0.12-0.23
CH_4	nd-0.59
COS	nd-0.22

Biospheric and industrial sources

Carbon dioxide

Present concentration	:	344 ppmv ($\cong 741 \times 10^{15}$ gC)
Seasonal oscillation due to respiration and photosynthesis within biosphere	:	~ 5 ppmv (10.6×10^{15} gC Yr^{-1})
Fossil fuel	:	5×10^{15} gC Yr^{-1}
Deforestation—regrowth	:	2×10^{15}
Tropical agricultural burning	:	7×10^{15}
Sinks: Oceans	:	2.5×10^{15}
Atmospheric increase	:	2.5×10^{15}

Nitrous oxide

(McElroy and Wofsy, 1985; 1984 concentration 303 ppb):

Atmospheric burden	:	1500×10^{12} g N
Sources: Oceans	:	$2 \pm 1 \times 10^{12}$ g N Yr^{-1}
Combustion (Coal + Oil 4 ± 1) :		4.7 ± 1.2
(biomass 0.7 ±0.2)		
Fertilized agricultural fields	:	$0.8 + 0.4$
Grasslands	:	< 0.1
Boreal and temperate forests	:	0.1-0.5
Tropical and subtropical forests and woodlands	:	7.4 ± 4
Total	:	15.3 ± 6.7
Sinks: Stratospheric photolysis and reaction with $O(^1D)$ e.g. $N_2O + h\upsilon \longrightarrow N_2 + O$ $N_2O + O(^1D) \longrightarrow 2NO$ or $N_2 + O_2$	:	10.5 ± 3
Accumulation (0.7 ppb/Yr^{-1})	:	3.5 ± 0.5
Total	:	14.0 ± 3.5

Tropical contribution:

Biomass burning	:	0.6	
Soil emissions	:	7.4	
Total	:		8.0

Special points: Soils in tropical forests emit N_2O flux 10 times larger than others:

Tropical forests	:	2×10^{10} N_2O cm^{-2}s^{-1}
Other forests	:	$1\text{-}2 \times 10^9$
Agricultural soil	:	2×10^9

Methane

Sources (Khalil and Rasmussen, 1983)

Enteric fermentation (cattle, sheep, etc.)	:	$100\text{-}150 \times 10^{12}$ g CH_4 Yr^{-1}
Rice paddies	:	100 ± 50
Wetlands	:	150 ± 50
Biomass burning	:	$10 - 60$
Others	:	$10 - 150$

Sinks (McElroy and Wofsy, 1985; 1984 concentration 1630 ppb):

Reaction with OH	:	$425 \pm 125 \times 10^{12}$ g CH_4 Yr^{-1}	
Uptake by dry soils	:	10 ± 5	
Accumulation (20 ppb Yr^{-1})	:	60 ± 15	
Total	:		495 ± 145

TROPOSPHERIC-STRATOSPHERIC SYSTEM

We limit ourselves to: (i) ozone problem; and (ii) greenhouse molecules.

Ozone chemistry

Ozone chemistry, since the classical work of Chapman, has gone through many complex changes, especially with the recognition of the role of catalytic radical species

HO_x, NO_x, ClO_x, all essentially brought into the stratosphere from tropospheric sources: NO_x from subsonic and supersonic aircrafts, N_2O from agricultural and combustion practices, CFCs from aerosol propellants, blowing agents and refrigerants.

The catalytic action of these radicals is similar and can be expressed as below:

$$X + O_3 \longrightarrow XO + O_2$$

$$XO + O \longrightarrow X + O_2$$

Net: $$O + O_3 \longrightarrow 2O_2$$
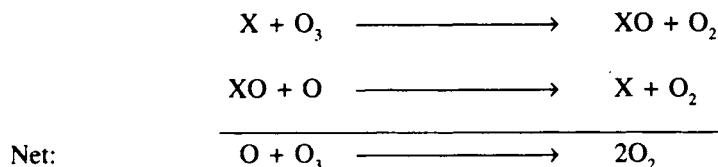
where the catalyst X could be one or more of the following:

$$X = H, OH, NO, Cl, Br$$

Ozone scheme, from current knowledge, can be summarised as in Fig. 14.

Chapman theory (Oxygen-only atmosphere) — In this pioneering initial ozone chemistry, Chapman suggested the following sequence of reactions (see Fig. 3).

Production
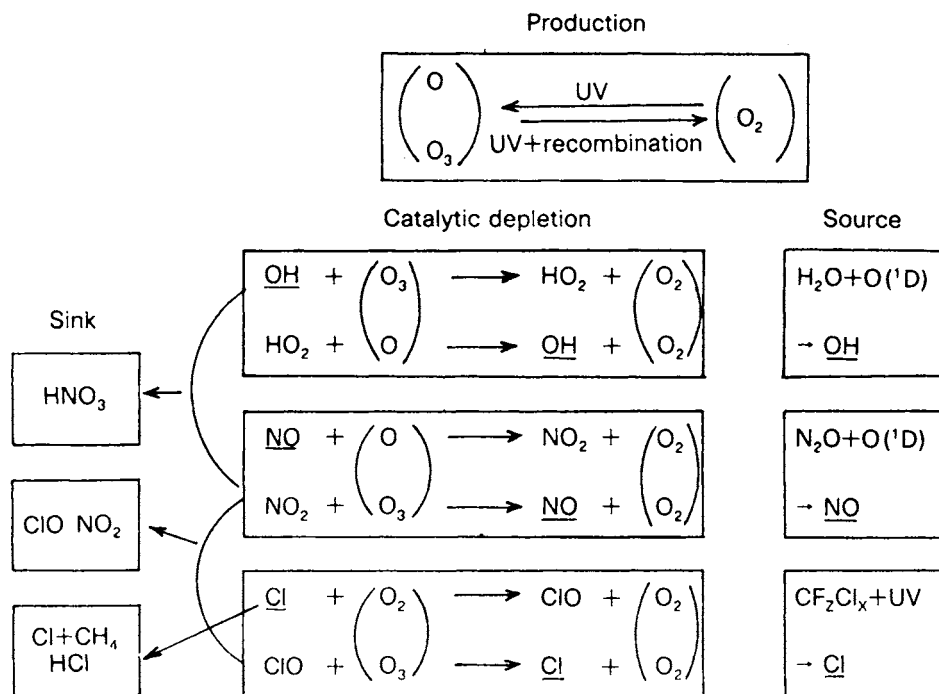
Fig. 14. Coupling between OH, NO and Cl.

$$O_2 + h\upsilon \xrightarrow{\;< 242 \text{ nm}\;} O + O \text{ (primarily above 20 km)} \quad \ldots (1)$$

followed by:

$$O + O_2 + M \longrightarrow O_3 + M \qquad \ldots (2)$$
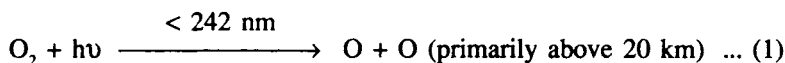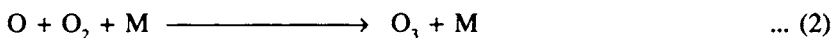
Ozone in turn is dissociated by:

$$O_3 + h\upsilon \longrightarrow O_2 + O(^1D) \qquad \ldots (3)$$

$$O(^1D) + O_3 \longrightarrow 2O_2 \qquad \ldots (4)$$
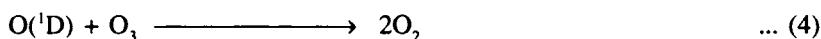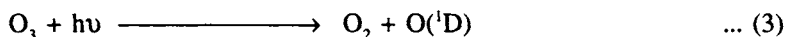
Hydrogen system—The OH system destroys only 10 % of O_2 but is dominant above 40 km.

$$H_2O + O(^1D) \longrightarrow 2\ OH$$
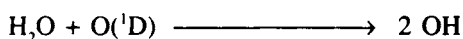
Reactions particularly important *above 40 km*:

$$OH + O_3 \longrightarrow HO_2 + O_2$$

$$HO_2 + O \longrightarrow OH + O_2$$

Net:$\quad\overline{\quad O + O_3 \longrightarrow 2O_2 \quad}$
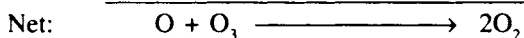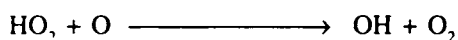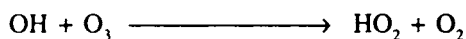
OH can also be formed from oxidation of methane:

$$CH_4 + O(^1D) \longrightarrow CH_3 + OH$$
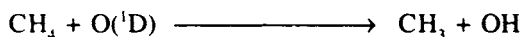
with subsequent reactions as above.
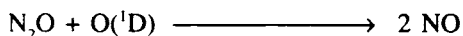
H, OH, HO_2 interconvert rapidly by reactions with O, so that all three tend to be in steady state. The scavenging reaction is:
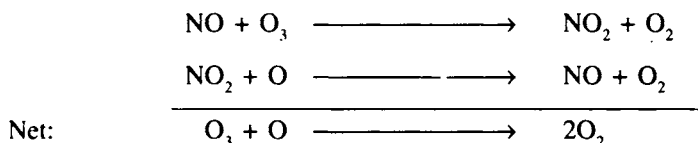
$$OH + HO_2 \longrightarrow H_2O + O_2$$
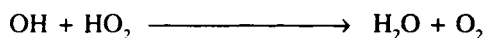
resulting in formation of H_2O which drifts down out of stratosphere. Since this reaction removes odd hydrogen out of the active system, its rate is one of the most important elements in stratospheric chemistry.

Nitrogen system—Sixty percent of ozone destruction occurs through this system. The sequence is as follows:

N_2O produced by bacterial action of micro-organisms in ocean and soil (denitrification) diffuse upwards from troposphere to stratosphere, where

$$N_2O + O(^1D) \longrightarrow 2\ NO$$

$$NO_2 + h\upsilon \longrightarrow NO + O$$
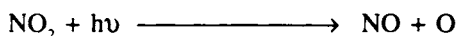
and NO so formed catalyses ozone by:

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

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

Net: $$O_3 + O \longrightarrow 2O_2$$

the reaction of NO_2 with OH:
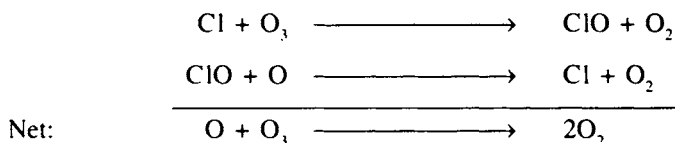
$$OH + NO_2 + M \longrightarrow HNO_3 + M$$

produces HNO_3 which is eventually washed out of the troposphere and is the major sink.

   Chlorine system—Natural chlorine contributes only very little (few percents) to O_3 destruction. CFM's (particularly $CFCl_3$ and CF_2Cl_2) are the main ozone destroyers. They are inert in the troposphere but get dissociated in the stratosphere:

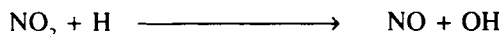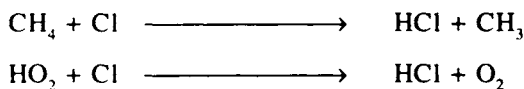$$CFCl_3, CF_2Cl_2 \xrightarrow[\text{180-220 nm}]{h\upsilon} Cl_2$$
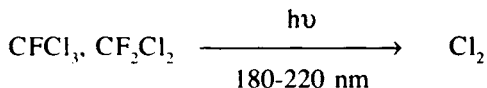
Then follow the following sequences:

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$ClO + O \longrightarrow Cl + O_2$$

Net: $$O + O_3 \longrightarrow 2O_2$$

ClO catalytic efficiency is *reduced* in presence of NO because of the reaction:

$$ClO + NO \longrightarrow NO_2 + Cl$$

followed by:

$$NO_2 + H \longrightarrow NO + OH$$

The sink is HCl, formed through:

$$CH_4 + Cl \longrightarrow HCl + CH_3$$

$$HO_2 + Cl \longrightarrow HCl + O_2$$

Chlorine can be recycled through:

$$HCl + OH \longrightarrow H_2O + Cl$$
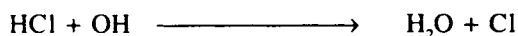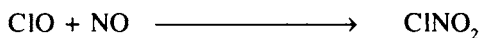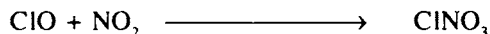
   Balance between Cl, ClO and HCl are given by the above three reactions.

While chlorine catalysis of ozone is six times as efficient, catalysis of ozone conversion to "inert" HCl is also more efficient than conversion of HNO_3; so that the overall efficiency of the two are comparable.
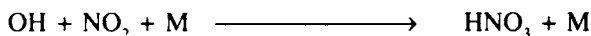
Again we have a coupling reaction:

$$ClO + NO \longrightarrow ClNO_2$$
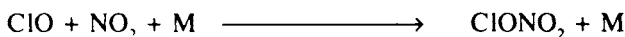
and

$$ClO + NO_2 \longrightarrow ClNO_3$$

It was thought at one time that this reaction reduces ozone depletion efficiency by other reactions from 14% to 7.5% (by a factor of 1.86). However, it seems that

$$OH + NO_2 + M \longrightarrow HNO_3 + M$$

is more efficient than

$$ClO + NO_2 + M \longrightarrow ClONO_2 + M$$

Reaction scenario—The three principal radical species OH, NO and Cl coming primarily from H_2O, N_2O and CF_xCl_y respectively and interacting with ozone catalytically eventually end up as sink species HNO_3, $ClONO_2$ and HCl. A summary scenario is shown in Fig. 14.

Antarctic ozone hole—The homogeneous chemistry described above is inadequate for the large depletion seen in the Antarctic and now in the Arctic. Prior to the discovery of the Antarctic ozone hole, the conclusion that was emerging was of a statistically insignificant change (so far) in ozone content and of recognizable changes only at upper stratospheric levels around 40 km. Theoretical calculations, both 1-D and 2-D, also predict only a few percent of change of the total ozone content, and not the almost complete annihilation one sees over the Antarctica.

To understand the special chemistry obtaining in the Antarctic one should first understand the very special conditions under which the "hole" appears. These are:

   (i) Very low T ($-80°$ C and below);

  (ii) Presence of stratospheric clouds;

 (iii) ClO increase to values about 100 times larger than in mid-latitudes;

 (iv) Decrease of odd nitrogen; and

  (v) Chemically depleted region is dehydrated and denitrified.

The most important thing is to understand how ClO can be increased by such a large magnitude between 12 and 20 km over such a short period. The existing gas

phase chemistry (Fig. 15) would suggest that in this region chlorine exists primarily in a reservoir form as HCl, $ClONO_2$.
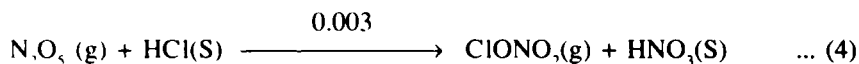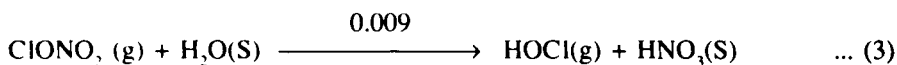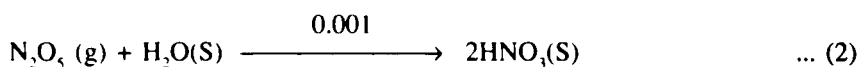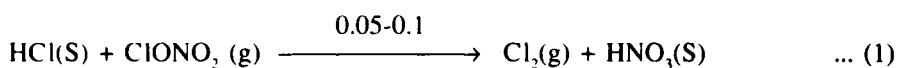
We have two alternatives. Either conditions occur which block the diversion of ClO into reservoir species or reactions occur that release ClO from the reservoir or both. An optimum condition would involve both *increase* in ClO and *decrease* in NO_x.

The key factor, it is believed, is the occurrence of extremely low temperatures. Such low temperatures promote increased occurrences of polar stratospheric clouds (PSC's). There are two types of PSC's:

| Type I | PSC | $-77°C$ | $HNO_3.3H_2O$ |
| Type II | PSC | $-85°C$ | Ice crystals |

Type I PSCs have particles of radii around 0.5-0.7 μm and occur at temperatures about 5-7 K higher than the frost point (Type II). Type I temperature is consistent with thermodynamical stability of HNO_3, $3HNO$ (NAT). Type II water-ice type clouds form at temperatures below the frost point, leading to large scale irreversible removal of H_2O vapour in the Antarctic.

The key heterogeneous reactions are:

$$HCl(S) + ClONO_2 \text{ (g)} \xrightarrow{\text{0.05-0.1}} Cl_2(g) + HNO_3(S) \quad \dots (1)$$

$$N_2O_5 \text{ (g)} + H_2O(S) \xrightarrow{\text{0.001}} 2HNO_3(S) \quad \dots (2)$$

$$ClONO_2 \text{ (g)} + H_2O(S) \xrightarrow{\text{0.009}} HOCl(g) + HNO_3(S) \quad \dots (3)$$

$$N_2O_5 \text{ (g)} + HCl(S) \xrightarrow{\text{0.003}} ClONO_2(g) + HNO_3(S) \quad \dots (4)$$

The sticking coefficients measured by Leu *et al.* (1988) and others show that these coefficients are appreciable.

These reactions provide pathways for removal of NO_2, thus inhibiting $ClO + NO_2 \longrightarrow ClO\ NO_2$ pathway and also releasing Cl_2 (g) as in (1) for PSC Type I and $HOCl$ as in (3) for ice-clouds of PSC Type II. Fig. 15 indicates diagrammatically such possibilities.

Model calculations using the set of heterogeneous reactions outlined above by Salawitch *et al.* (1988). profiles of Cl_x appropriate for each year since 1960 (1.0 ppb in the upper stratosphere for 1960, 1.50 ppb for 1970, 2.4 ppb for 1978, 3.3 ppb for 1985). and with several assumptions regarding duration of PSCs and of different percentages of return of condensed HNO_3 to gas phase, showed that about 50% reductions are possible for Cl concentration above 2.4 ppb (1978 level) with
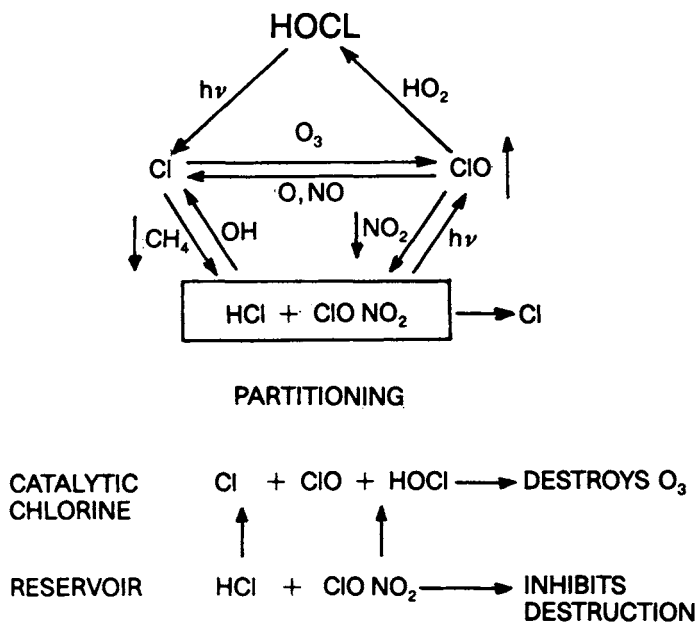
Fig. 15. Antarctic ozone chemistry.

temperatures below condensation point of water occurring for an extended period of time and with more than 80% of HNO_3 removal.

A new result of major implication is that such surface reactions are not limited to ice-clouds, but can also occur on liquid sulfuric acid aerosols. These occur at higher temperatures. Laboratory measurements have been reported on interactions of $ClONO_2$, HCl and HNO_3 on 65-75% H_2SO_4 solutions at temperatures between −63° to −43°C. These provide possibilities of ozone reduction at *lower* latitudes and provide the first evidence for possible ozone reduction at latitudes outside the Antarctic and the Arctic.

An example of ozone depletion from sulfate aerosol particles is provided by volcanic eruptions. An example was the eruption of EL Chichon in 1982 ejecting a large amount (3-8 × 10^{12}g) of SO_2 in the atmosphere (Hofman and Solomon, 1989). Following this eruption O_3 concentration was depleted by about 15% between 10° and 50°N.

Greenhouse molecules

The important greenhouse molecules, in concentrations in 1979 and 1986 (solar maximum and solar minimum respectively), rate of growth calculated lifetimes are shown in Table 2:

TABLE 2: Greenhouse Molecules

Species	Mixing ratio			Recent rate of growth (%/yr)	Calculated lifetime	Ozone depletion potential[b]	HGWP[c]
	1979	1986	2050[a]				
CO_2	335.5ppm	344.0	(600)	0.5	—	—	—
CH_4	1.62ppmv	1.70	(3.3)	1	6.5	—	—
N_2O	305ppbv	310	(600)	0.25	170	—	—
F11	170pptv	220	(673)	5	70	1.0	1.0
F12	290pptv	390	(1325)	5	144	0.9	3.4
F22	50pptv	87	(631)	11.7	17	0.05	0.35

Note:

a   Values for 2050 are on the basis of constant atmospheric emissions on Montreal products after 1985, using 1986, production as the atmospheric flux, for other trace gases using a linear rate of change and for CFC-22 to grow linearly by an additional 76g/year after 1985.

b   Hydrocarbon Global Warming Potential relative to F11.

c   Relative to F11.

The biosphere produces these gases in variety of ways. These are shown below (all in g.Yr^{-1}):

(i) Biomass burning

CO	$4\text{-}16 \times 10^{14}$g
CH_4	$0.3\text{-}11 \times 10^{12}$ g
NO_x	$10\text{-}14 \times 10^{12}$g N
N_2O	$1\text{-}2 \times 10^{12}$ g N
NH_3	$< 60 \times 10^{12}$ g

(ii) Rice paddy fields

CH_4	$100 \pm 50 \times 10^{12}$g CH_4

(iii) Fertilized fields, cultivations, soils

NO_x	$1\text{-}15 \times 10^{12}$ g
NH_3	$< 0.35 \times 10^{12}$ g
N_2O	0.8×10^{12} g

(iv) Enteric fermentation (cattle, sheep, etc.)

NH_3 $12\text{-}26 \times 10^{12}$ g
CH_4 $100\text{-}150 \times 10^{12}$ g

(v) Oceans and estuaries

N_2O $2 \pm 1 \times 10^{12}$g N
NO_x ($NO + NO_2$) 0.2×10^{12}g N

The history of these gases, in their sojourn through the troposphere and stratosphere, going through a number of reactions is shown in Fig. 16 (Crutzen, modified).
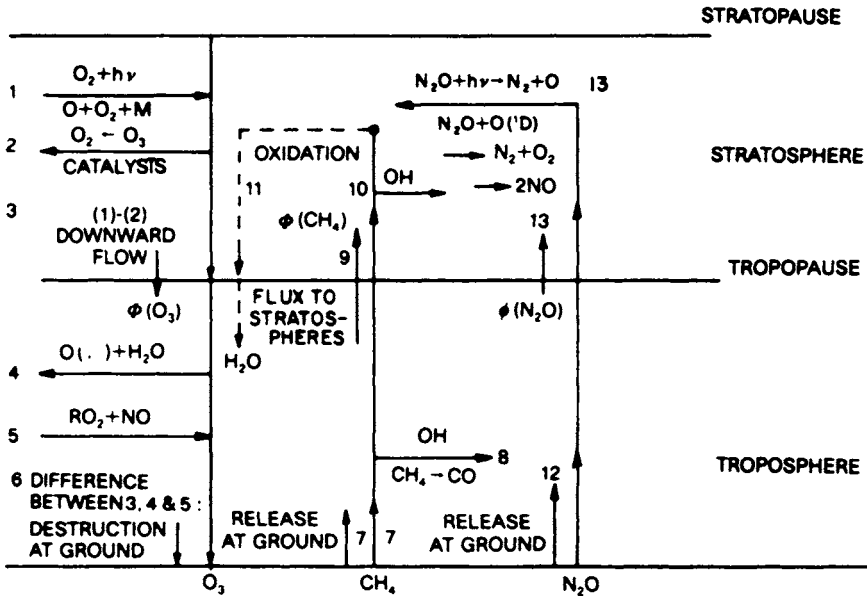

Fig. 16. Pathways of selected greenhouse molecules.

IONOSPHERIC MODIFICATIONS

As earlier mentioned, effects of human activities are not limited to the troposphere and the stratosphere—there are effects at much greater heights extending perhaps to tens of thousands of kilometers. The three major sources of perturbations in the upper stratosphere are:

(i) Spacecraft effluents;

(ii) Heating of the ionosphere by high power transmitters; and

(iii) Effects of power lines.

Of these chemical reactions are particularly dominant for spacecraft effluents. We will limit ourselves here only to this area.

Spacecraft effluents

These are of two kinds:

(i) Materials released as rocket exhausts; and

(ii) Materials released deliberately from the rocket as a tracer (the so-called "release" experiments).

Historically the first experiment of "modifying" the upper atmosphere was through "release" experiments. One of the best known experiments was the "Argus" during IGY when artificial radiation belts were produced by three nuclear test explosions 480km above the earth on August 29 and 30 and September 6, 1958 over the South Antarctic Ocean. Following the explosions a fascinating sequence of observations were observed: the brilliant initial flush of the explosion was followed by a fainter but persistent luminiscence along the magnetic lines of force through the burst point. Almost simultaneously a bright auroral cloud appeared at the conjugate point. A new radiation belt was produced.

The second well-known experiment was "West Ford"—a highly controversial experiment. In this a large number of their microwave dipoles (75 pounds) were placed in orbit around the earth as a scattering medium for radio signals in the Centimeter band.

However, those that have principal interest in the context of this address are the "Ionospheric holes" produced by rocket exhausts, because these involve chemically interactive processes. A list of these and the effects produced are summarised below:

(i) Golomb & Rosenberg	Expt. I:	150 moles of SF_6:220 km
	Expt. II:	130 moles of CO_2:220km
(ii) Project Firefly	1962	5.44 kg CO_2 at 234 km
(iii) Starfish	1962	To disturb van Allen Belts disturbances long-enduring
(iv) Skylab I	1973	H_2, H_2O from Rocket Exhausts: a total of 1.2×10^{31} molecules spread over 1800 km

    (v) Lagopedo   1977   38 kg of H_2O, 16 kg of CO_2, 20 kg of N_2

    (vi) HAEO-C   1979   Well planned experiment 7×10^{29} H_2O and H_2 molecules burnt from 211-501 km

In all these cases the effects were of *reduction* of ionization in the ionospheric F-region over varying areas. In the Golomb-Rosenberg experiments reduced electron densities were observed after a lapse of few minutes, lasted for 30 minutes for SF_6 release and 3 minutes for CO_2 releases. The Skylab effects, which come as a surprise, were unique in magnitude and spatial extent: a large "hole" was observed extending over an area of about 1000 km (seen through satellite TEC experiments). Lagopedo and HAEO-C experiments were planned experiments. In Lagopedo a hole extending over a radius of 30km was observed lasting for 30 minutes. In the HAEO-C experiment the hole was formed within a few seconds, was 2500 km long and 800 km wide and 300-400 km thick. There was nearly 100% depletion of electrons within 75 km of the trajectory during the maximum effect. The hole persisted until shortly after sunrise some 4 hours after launch. There were major radio effects of this depletion: VLF showed appreciable phase changes, HF signals recorded after the launch were low with increased fading.

Although there are several theories, the most reasonable (but not necessarily the only one) is that attributed to increased recombination through sudden deposition of a large quantity of H_2O and H_2 in the upper atmosphere. There are two specific levels we will consider: (i) at the level of the D-region ledge around 85 km and (ii) in the F-region. In a very simplistic way the expected concentration change = (Injection rate) × (Residence time). The residence time is given by: (Residence time)$^{-1}$ = Transport removal rate + Chemical removal rate.

Normally around the ledge height the dominance of the water cluster ions disappears with NO^+ and O_2^+ being the principal ions above these levels. Recombination of these ions occur through:
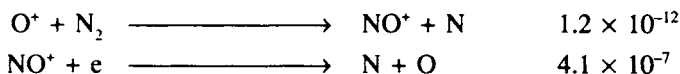
$$NO^+ + e \longrightarrow N + O \qquad 4 \times 10^{-7}$$
$$O_2^+ + e \longrightarrow O + O \qquad 2 \times 10^{-7}$$
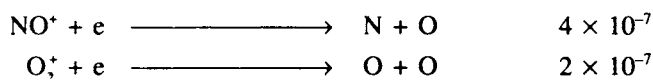
When H_2O concentrations are increased, the region 80-100 km gets changed into heavier clusters - dominated region from the predominant NO^+, O_2^+ regions. These clusters ions have 10 to 100 times larger recombination coefficients (10^{-6} to $10^{-5} cm^3 s^{-1}$), depending on the degree of clustering. Consequently a reduction of N_e occurs. If an increased H_2O mixing ratio of 100 ppmv is assumed, then the conversion of simple molecular ions to cluster ions is complete at 70-100 km levels. At the same time there is a reduction in UV radiation through screening by the increased water vapour concentration. An estimated reduction in daytime N_e from the combined effects is 75%. We may also note that although lifetimes of ions at
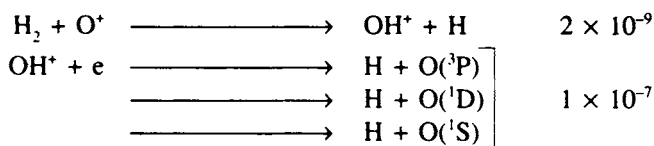
these heights are short—of the order of seconds and minutes — the relevant water molecules have lifetimes of about 35 days at 85 km and 15 days at 100 km, long enough to be distributed over the globe.

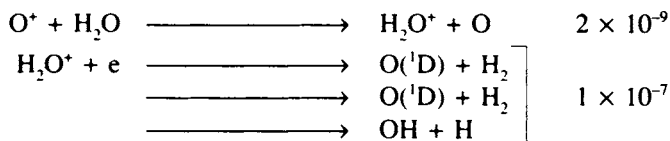The depletion is the most pronounced in the F-region. The chemistry here is as follows:

(i) Normal F_2 region dissociative recombination

$$O^+ + N_2 \longrightarrow NO^+ + N \qquad 1.2 \times 10^{-12}$$
$$NO^+ + e \longrightarrow N + O \qquad 4.1 \times 10^{-7}$$

(ii) Enhanced recombination with H_2

$$H_2 + O^+ \longrightarrow OH^+ + H \qquad 2 \times 10^{-9}$$
$$OH^+ + e \longrightarrow H + O(^3P) \left.\begin{array}{l} \\ \end{array}\right.$$
$$\longrightarrow H + O(^1D) \left.\begin{array}{l} \\ \end{array}\right\} \qquad 1 \times 10^{-7}$$
$$\longrightarrow H + O(^1S) \left.\begin{array}{l} \\ \end{array}\right.$$

(iii) Enhanced recombination with H_2O

$$O^+ + H_2O \longrightarrow H_2O^+ + O \qquad 2 \times 10^{-9}$$
$$H_2O^+ + e \longrightarrow O(^1D) + H_2 \left.\begin{array}{l} \\ \end{array}\right.$$
$$\longrightarrow O(^1D) + H_2 \left.\begin{array}{l} \\ \end{array}\right\} \qquad 1 \times 10^{-7}$$
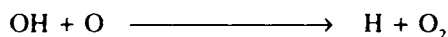$$\longrightarrow OH + H \left.\begin{array}{l} \\ \end{array}\right.$$

$O^+ + H_2$ or $O^+ + H_2O$ reactions are 10^3 times faster than $O^+ + N_2$ or $O^+ + O_2$ reactions. Furthermore, the OH radical formed through $H_2O^+ + e$ reaction can react further with O^+ through:

(i) $$O^+ + OH \longrightarrow O_2^+ + H$$

followed by:

(ii) $$O_2^+ + e \longrightarrow O(^1D) + O$$
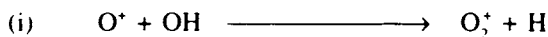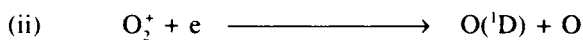
In most cases, however, the OH radical is destroyed by reaction with O through:

$$OH + O \longrightarrow H + O_2$$

before the charge transfer reaction can occur.

If H_2O flux injected by the rocket is high in comparison with ambient ion concentrations, then a number of reactions occur that compete with the earlier reactions. These are:
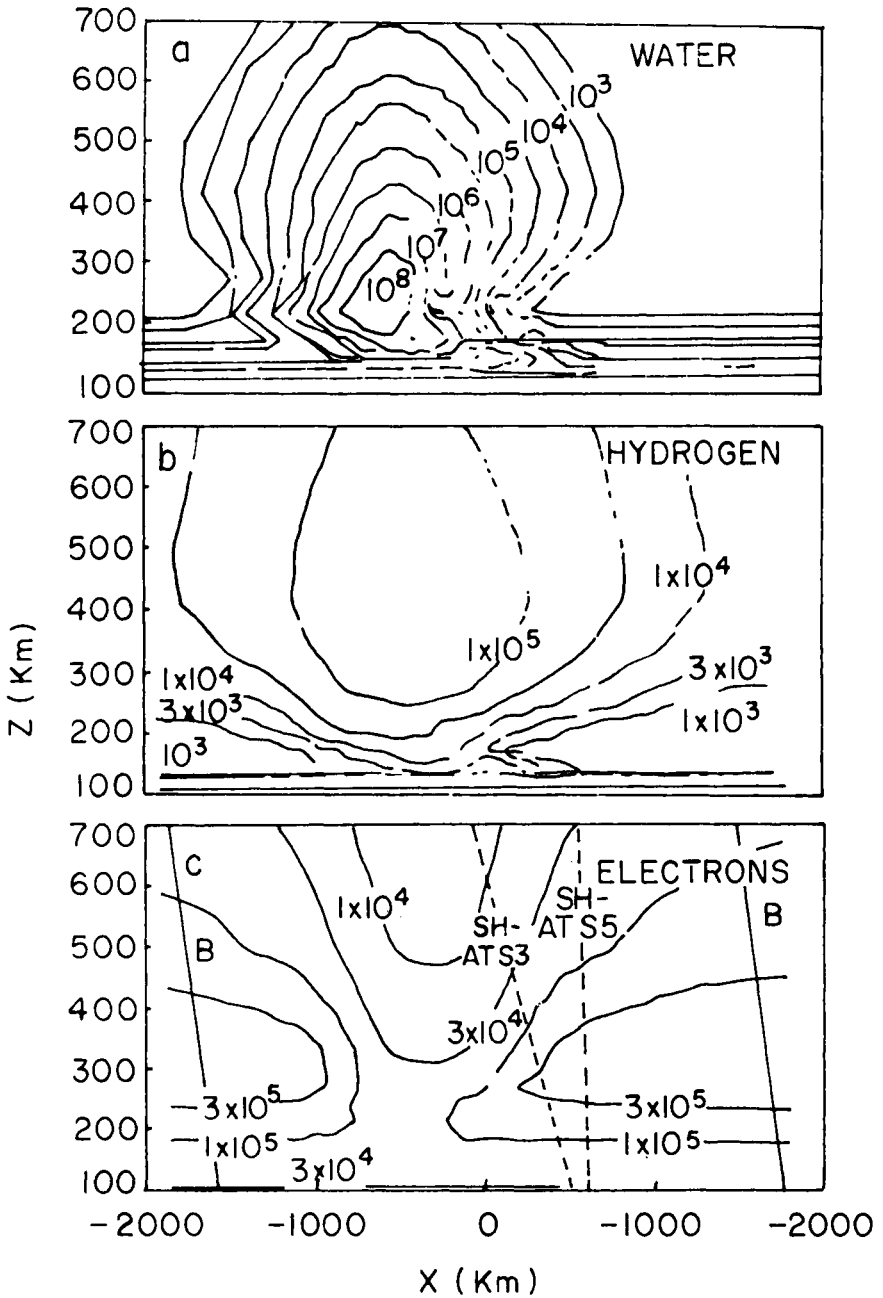
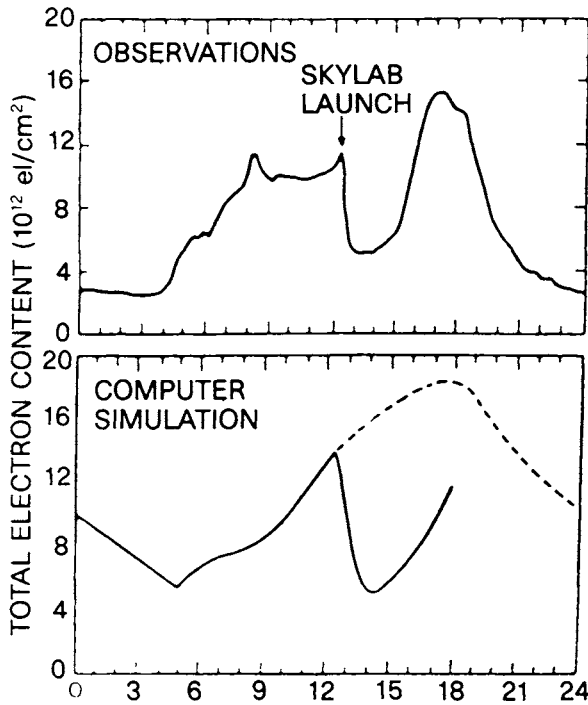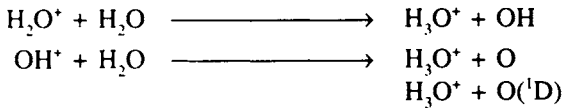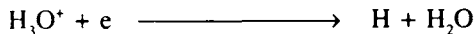Fig. 17a. Modelling of ionospheric hole from Skylab I.

Fig. 17b. TEC (Total Electron Content) changes—observed and modelled.

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH$$

$$OH^+ + H_2O \longrightarrow H_3O^+ + O$$
$$H_3O^+ + O(^1D)$$

followed by:

$$H_3O^+ + e \longrightarrow H + H_2O$$

The strong ion-removal effects by then exhaust particles are confined to heights above 200 km where ions are primarily atomic (O^+) and not below (dominated by molecular ions). The lifetime and the nature of the effect is determined by the residence times of the injected molecules. The time required for an H_2O molecule to fall from 400 to 200 km is about 2 hours. For hydrogen, although there is a tendency to settle, its behaviour is controlled by diffusion. H_2 cloud spreads 4 times as fast as H_2O cloud, but its setting rate is three times slower. Computer modelling of the "ionosphere hole" produced by Skylab along with the observed "hole" is shown in Fig.17 a,b

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