

Chemistry of Atmospheres: Notes for lecture 1

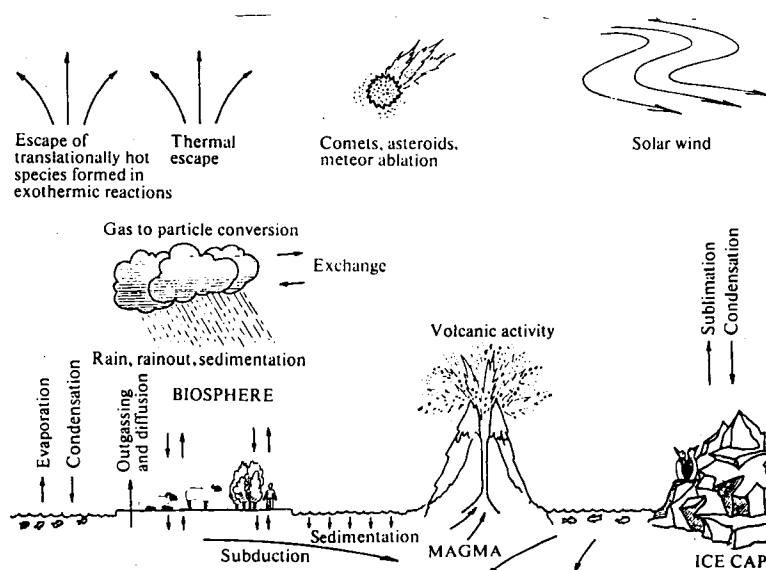
1.1 Major constituents of Earth's atmosphere (dry) at sea level; concentrations at STP

Species	RMM	Percentage	Concentration (molecule cm ⁻³)
N ₂	28.02	78.08	2.098 × 10 ¹⁹
O ₂	32.00	20.95	5.629 × 10 ¹⁸
Ar	39.95	0.934	2.510 × 10 ¹⁷
CO ₂	44.01	0.36	9.672 × 10 ¹⁵

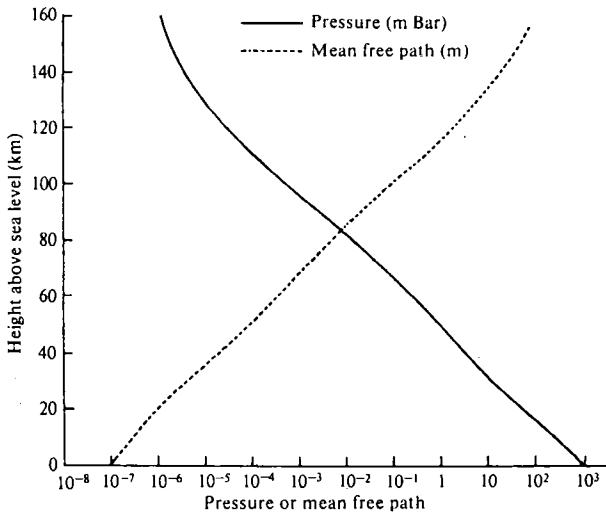
Total mass of Earth's atmosphere – 5 × 10¹⁸kg; 50% lies below 5.5km altitude, 99% below 30km.

1.2 Tropospheric gases

Species	Mixing ratio	Source/10 ⁹ kg yr ⁻¹	
		Man	Natural
CH ₄ , HCs	1.7 × 10 ⁻⁶ (CH ₄)	188	1800
CO ₂	0.36	2 × 10 ⁴	10 ⁶
CO	4 - 20 × 10 ⁻⁸	600	2500
N ₂ O	3.0 × 10 ⁻⁷		
NO _x	5 - 200 × 10 ⁻¹⁰	90	1200
NH ₃	<1 × 10 ⁻⁸	7	1200
SO ₂	1.1 × 10 ⁻¹⁰	207	~10
H ₂ S, CH ₃ SCH ₃ , CH ₃ SSCH ₃	1 × 10 ⁻¹⁰	2 (H ₂ S)	50 (H ₂ S)
COS	5 × 10 ⁻¹⁰		
H ₂ O	10 ⁻⁵ - 10 ⁻²		[weather]
O ₃	1 - 4 × 10 ⁻⁸	[chemistry]	[chemistry]



1.3 Representation of the cyclic processes of biogeochemistry that exchange constituents between air, land, and sea



1.4 Pressure and mean free path as a function of altitude.

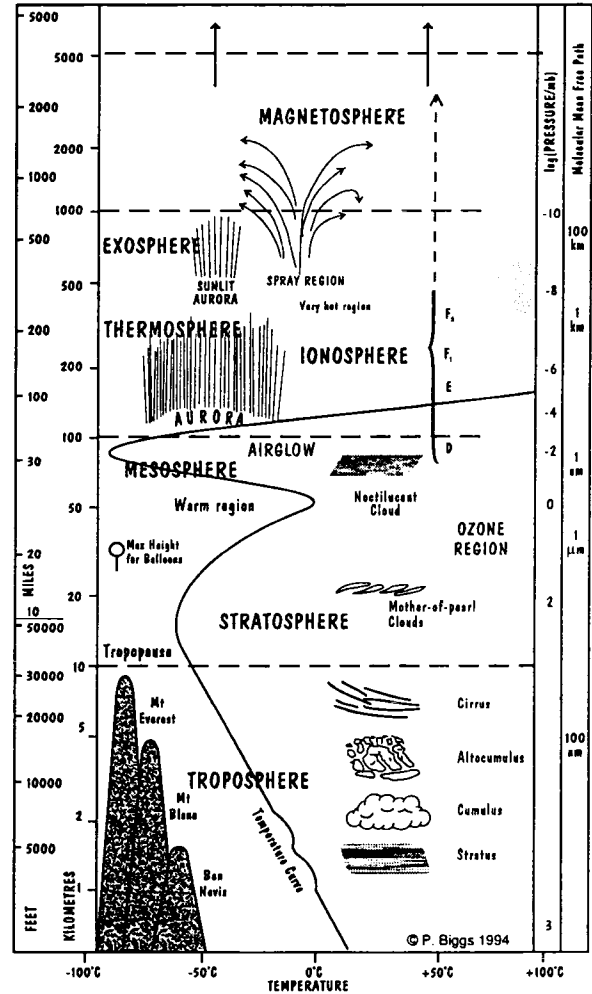
The hydrostatic equation is

$$\frac{dp}{p} = - \frac{dz}{(kT/mg)}$$

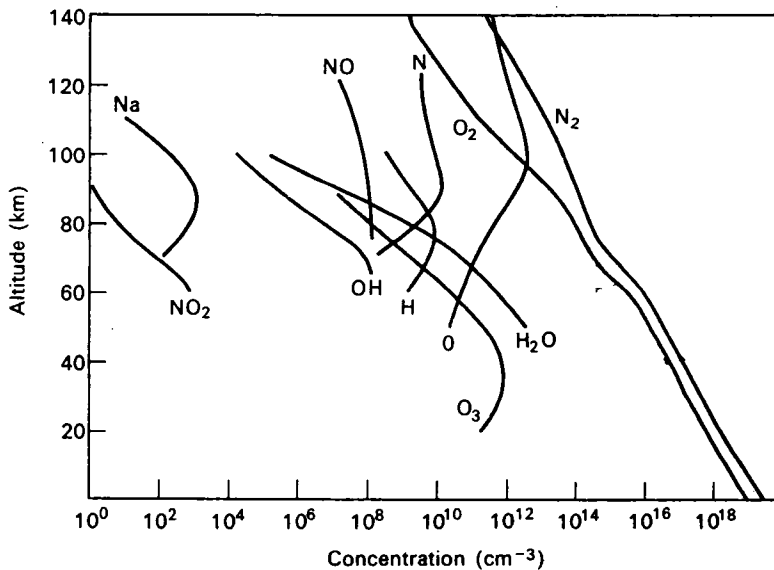
where p is the pressure, and z the altitude. For constant g and T , this equation can be integrated to

$$p = p_0 \exp(-mgz/kT)$$

The characteristic length $H = kT/mg$ is called the *scale height*, and is about 6 to 9km.



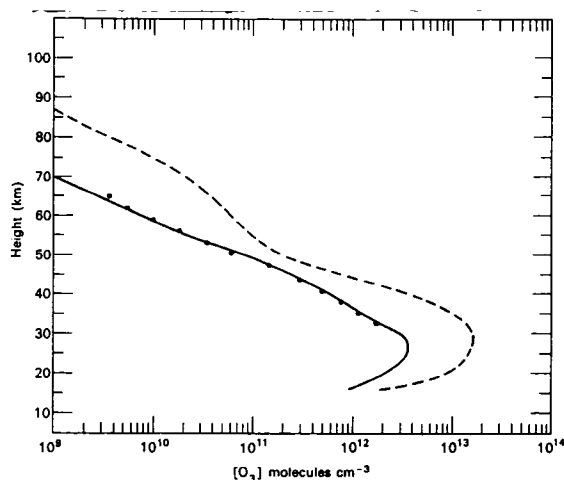
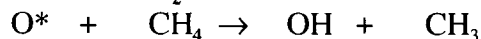
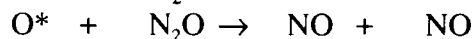
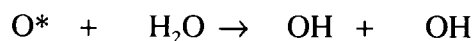
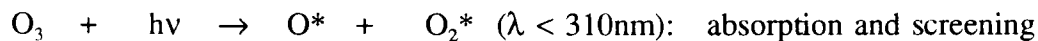
1.5 The temperature structure in the Earth's atmosphere and the atmospheric regions.



1.6 Representative concentration profiles of neutral species in the atmosphere

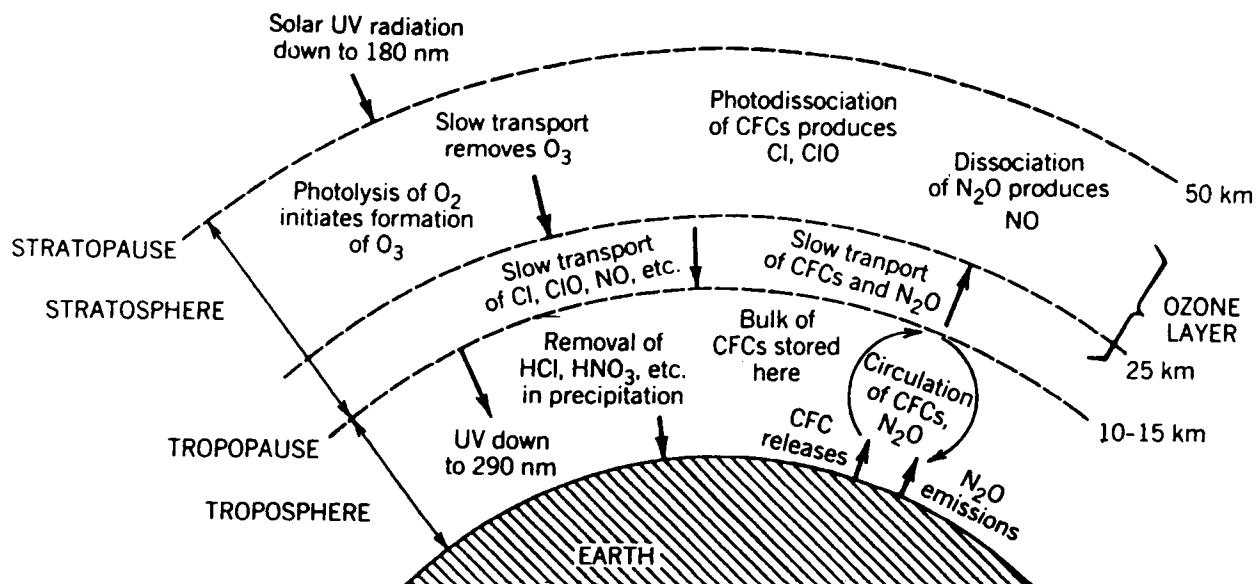
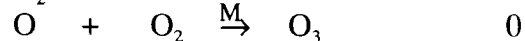
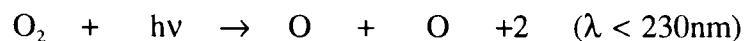
Chemistry of Atmospheres: Notes for lecture 2

2.1 The importance of ozone



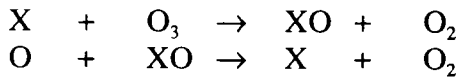
2.2 Ozone profile: measured and calculated (Chapman reactions only)

2.3 The Chapman reactions

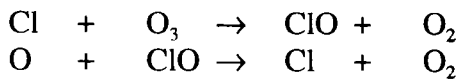
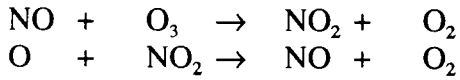
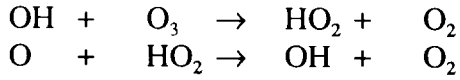


2.4 Chemistry involved in ozone formation and removal by trace catalysts

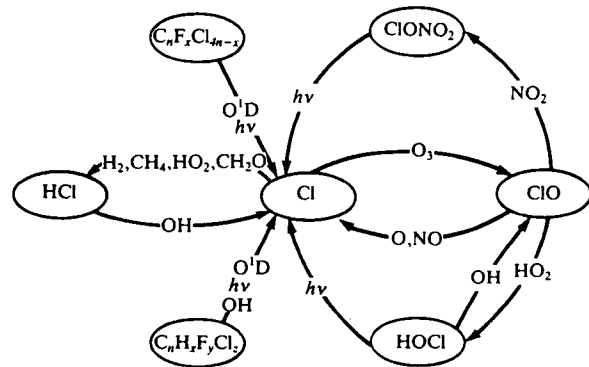
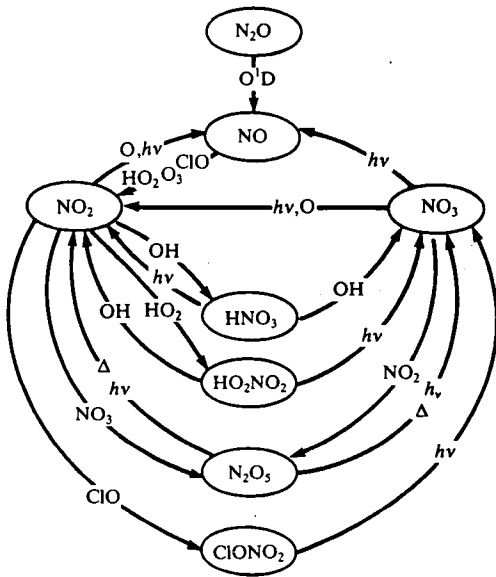
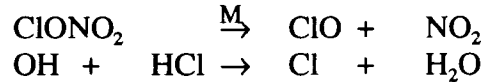
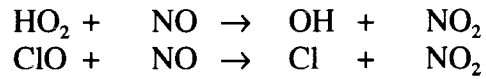
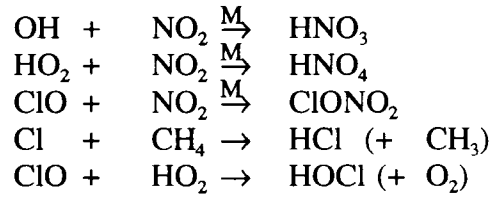
2.5 Catalytic cycles



X = OH, NO, Cl

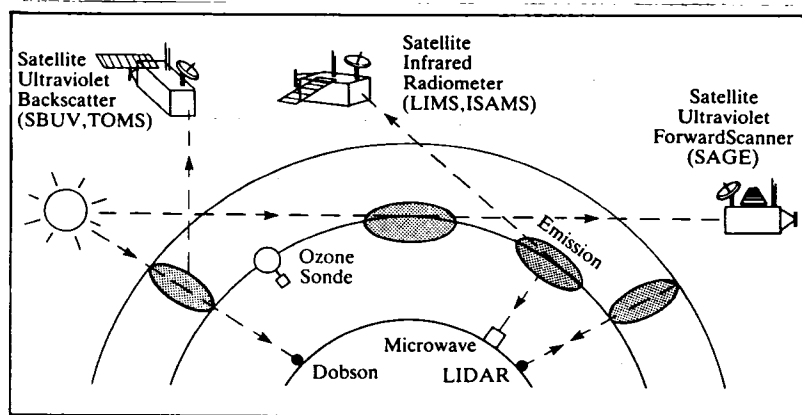


2.6 Reservoirs and cross cycles



2.7 Chemical cycles for NO_x species

2.8 Chemical cycles for ClO_x species



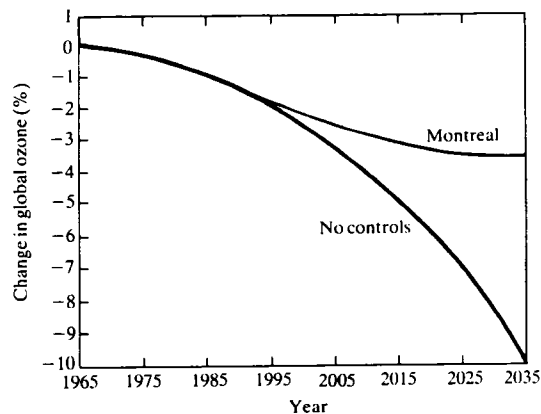
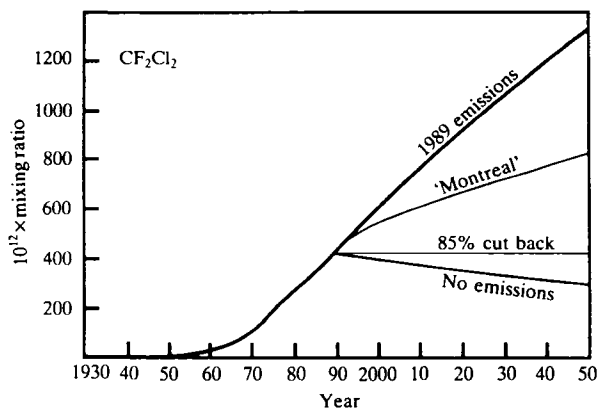
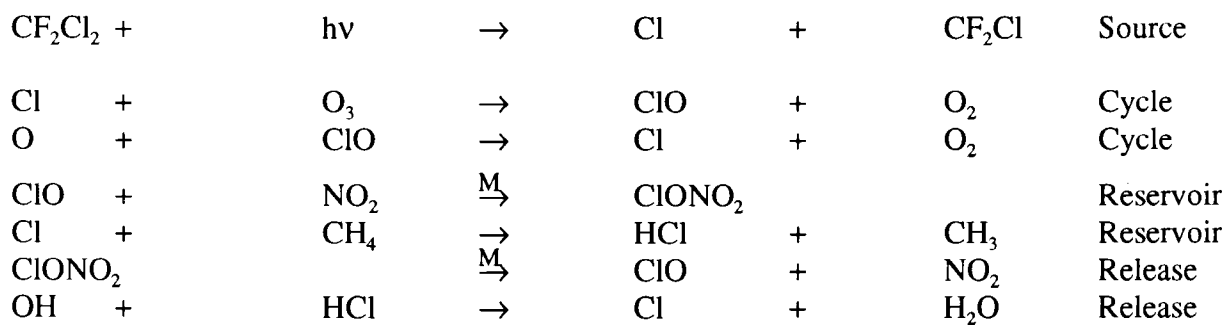
2.9 Some techniques for measuring stratospheric ozone concentrations

Chemistry of Atmospheres: Notes for lecture 3

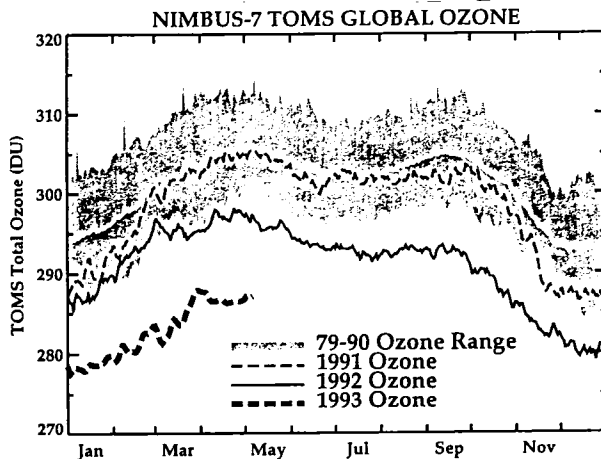
3.1 Sources of catalytic species

Family	X	XO	Sources	
HO _x	OH	HO ₂	O(¹ D) + H ₂ O	O(¹ D) + CH ₄
NO _x	NO	NO ₂	Lightning; ionosphere	O(¹ D) + N ₂ O
ClO _x	ClO	ClO	CH ₃ Cl + hv	CF ₂ Cl ₂ + hv, etc: MAN

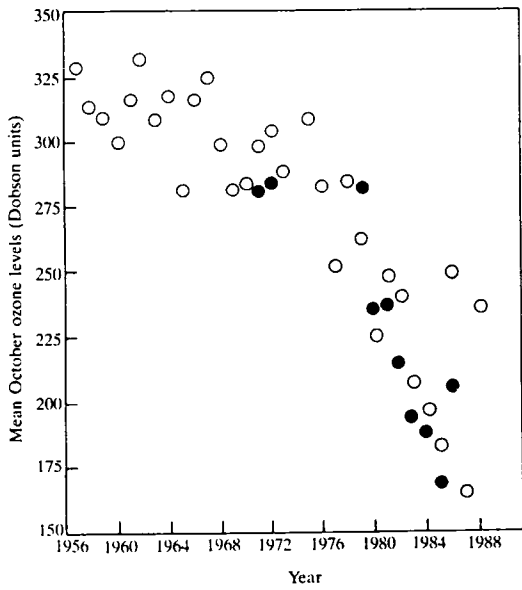
3.2 Reminder of chlorine chemistry



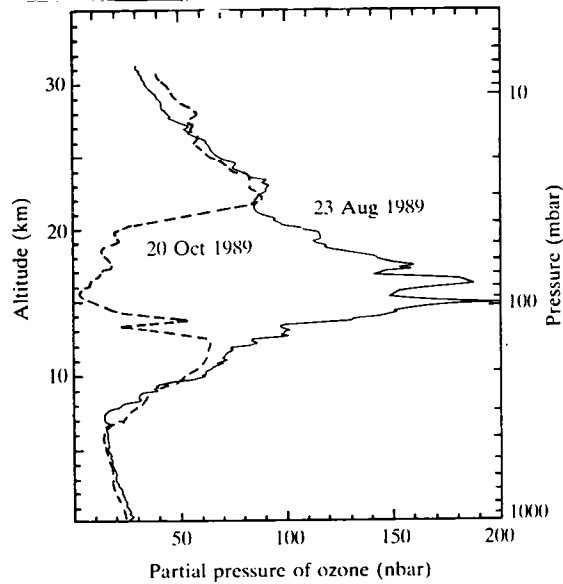
3.3 Projected time history of (a) CF₂Cl₂ concentrations; and (b) changes of ozone concentrations



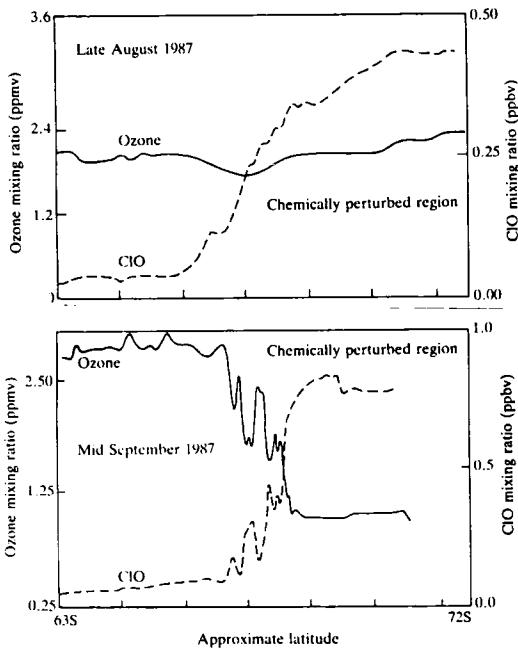
3.4 Recent TOMS measurements of zonally-averaged ozone, 30-60°N



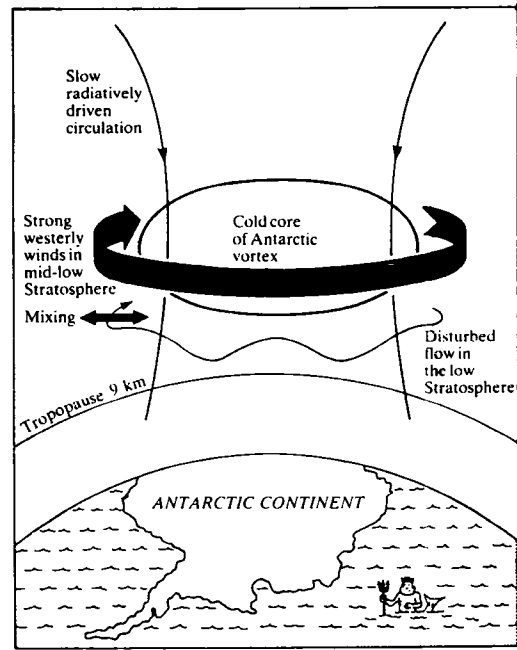
3.5 Decline in October [O₃], Halley Bay



3.6 Ozone height profiles in Antarctic, 1989

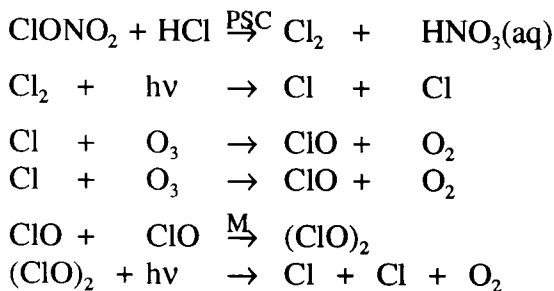


3.7 O₃ and ClO in August and September

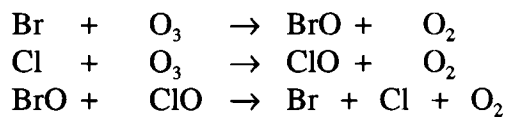
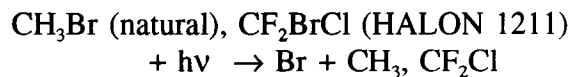


3.8 The Antarctic winter vortex

3.9 Ozone hole chemistry (chlorine)



3.10 Importance of bromine



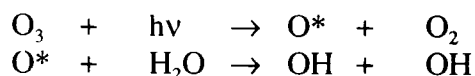
BrO + ClO → Br + OClO
is only known stratospheric source of OClO

All reservoirs of Br (BrCl, HBr, BrONO₂) are rapidly photolysed to regenerate X atoms.

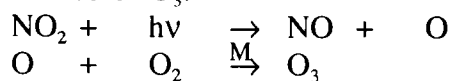
Chemistry of Atmospheres: Notes for lecture 4

4.1 Initial oxidation steps by day

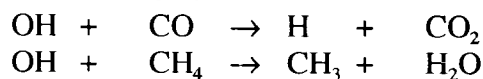
Initiation



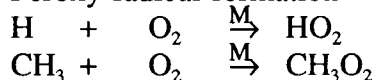
Source of O₃:



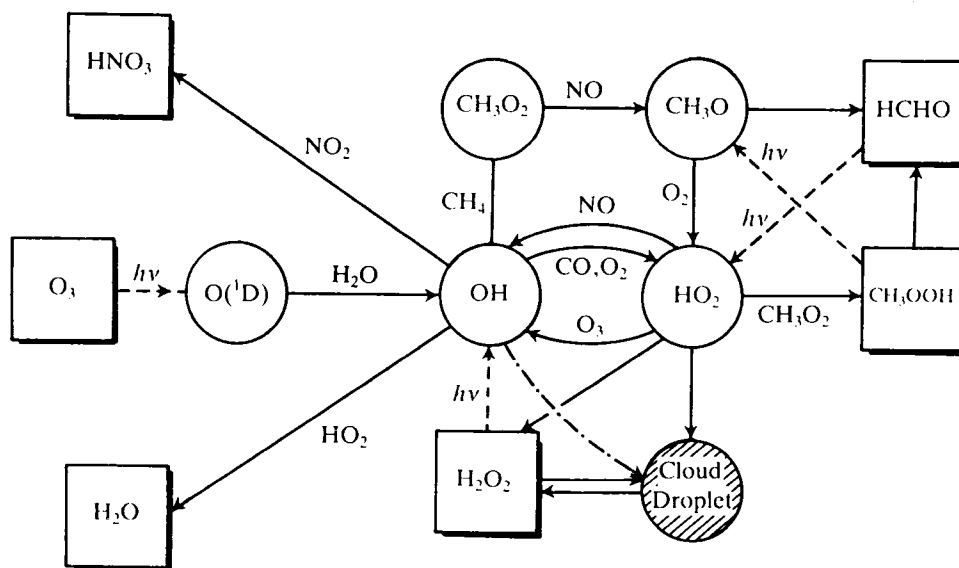
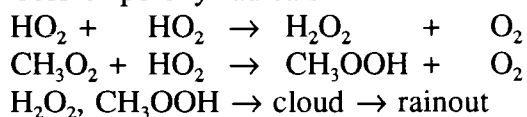
Attack of OH:



Peroxy radical formation



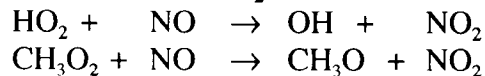
Loss of peroxy radicals



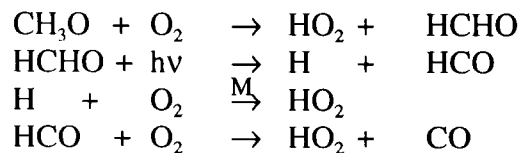
4.2 Chemistry of the troposphere

4.3 Cyclic processes: NO

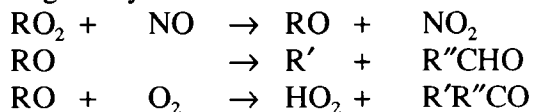
Conversion to NO₂:



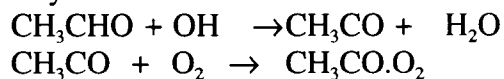
Fate of CH₃O:

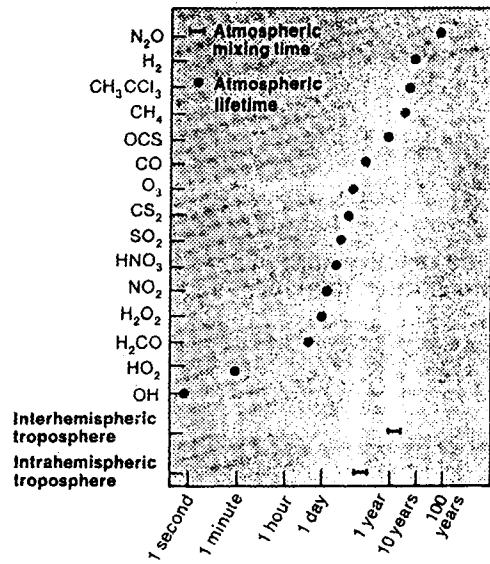
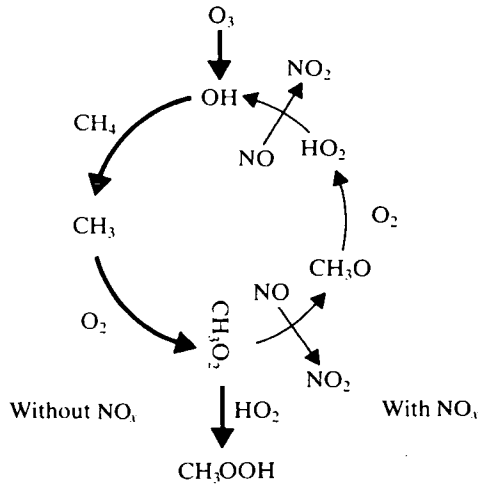


Higher hydrocarbons:



Acyl radicals:



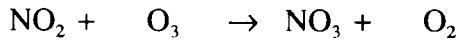


4.4 Importance of NO_x in methane oxidation

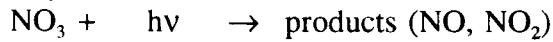
4.5 Atmospheric lifetimes of trace gases

4.6 The nitrate radical

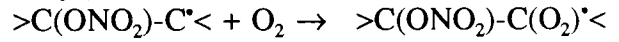
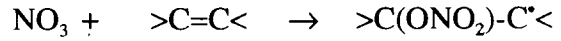
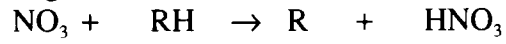
Formation:



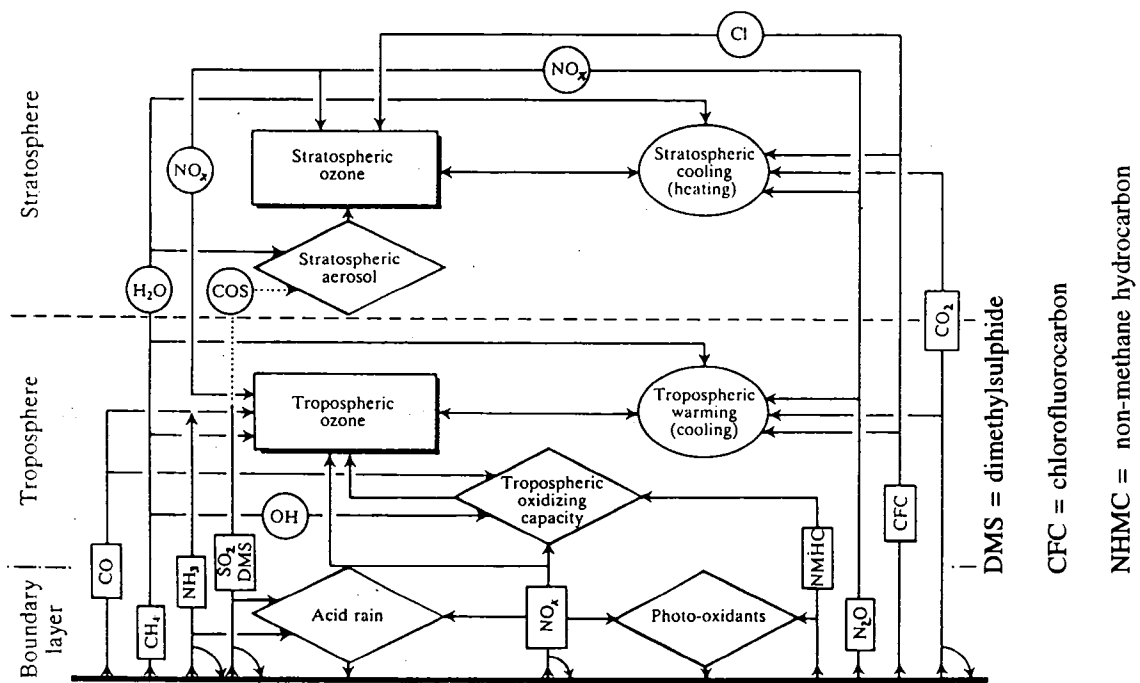
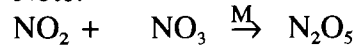
Daytime:



Night-time:

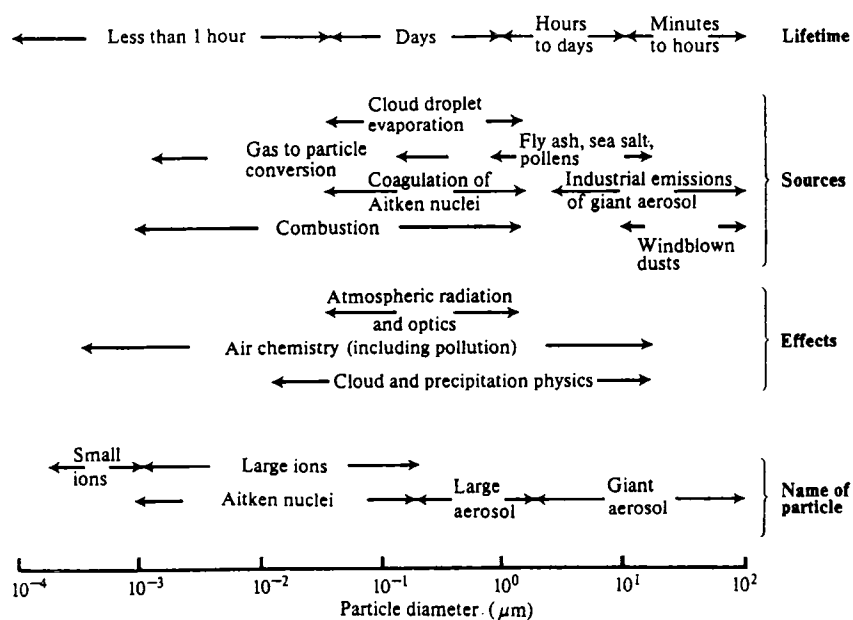


Note:



4.7 Feedbacks in atmospheric chemistry

Chemistry of Atmospheres: Notes for lecture 5



5.1 Effects, sources and lifetimes of atmospheric particles

5.2 Heterogeneous processes:

- (i) Condensation of single component;
- (ii) Reaction of gases to form particle;
- (iii) Reactions of gases on existing particle;
- (iv) Reactions within particles themselves.

Process (iii) - condensation of gases on pre-existing particles - is sometimes called *aerosol scavenging*. It affects bulk tropospheric chemistry by providing a sink for, eg, HNO_3 , NO_3 , N_2O_5 , H_2O_2 , HO_2 and organic nitrates and peroxides. "Rainout" removes these aerosols.

In process (iv), clouds offer a medium for aqueous-phase reactions, and have large influence on troposphere: Three reasons:

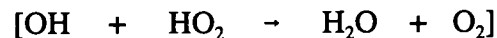
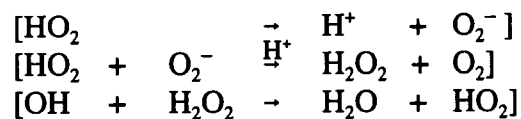
- (a) concentration in solution enhances rates (especially of 2nd order processes);
- (b) activation energies often less in solution than in gas phase; and, a **special feature**,
- (c) high solubility of certain key compounds such as HO_2 and N_2O_5 . Reactions of these species within droplet ensures that dissolution is irreversible and partitioning into aqueous phase is thus strongly favoured despite relatively small fractional volume of H_2O droplets (ca. 10^{-6})

5.3 Examples of droplet chemistry

Hydration of anhydrides

$[\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_3]$
 most important. Rate limited by gas-phase diffusion and transfer through interface.

Radical sinks:



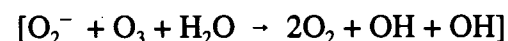
Thus oxidizing capacity of troposphere can be affected by droplet chemistry.

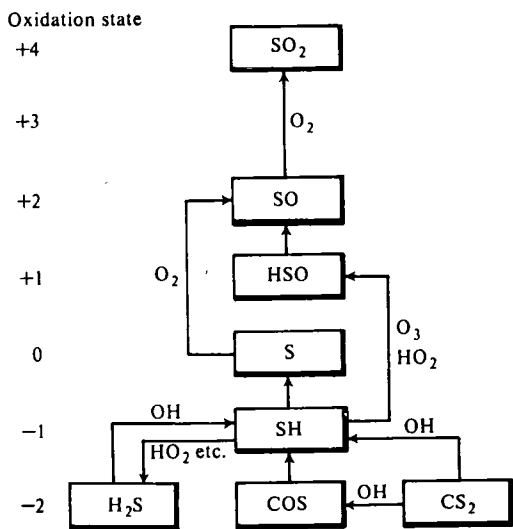
Because HO_2 is highly soluble, and NO is relatively *insoluble*, HO_2 and NO are separated by droplets, and the reaction



that ultimately yields O_3 in the gas phase is inhibited.

There are also reactions that destroy O_3 , such as

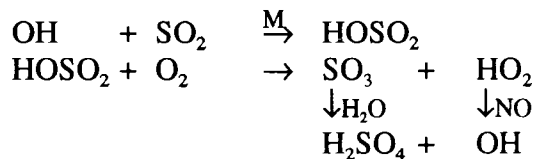




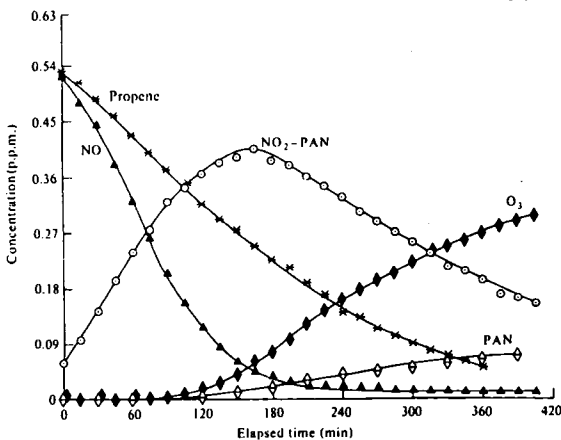
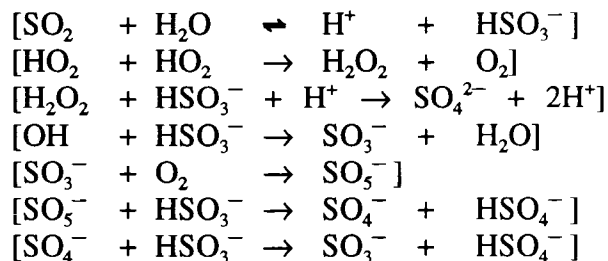
5.4 Oxidation of reduced S to SO₂

5.5 Oxidation of S(IV) to S(VI)

Gas phase:



Droplets:



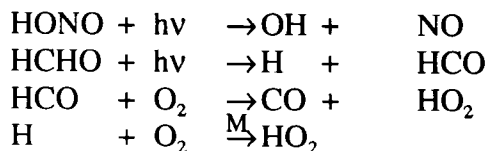
5.6 Smog chamber results

5.7 Photochemical smog chemistry

Exaggerated form of normal tropospheric oxidation: see notes 4.1 to 4.4 for the chemical steps.

Note that NO is converted NO₂, which is a photochemical source of O₃.

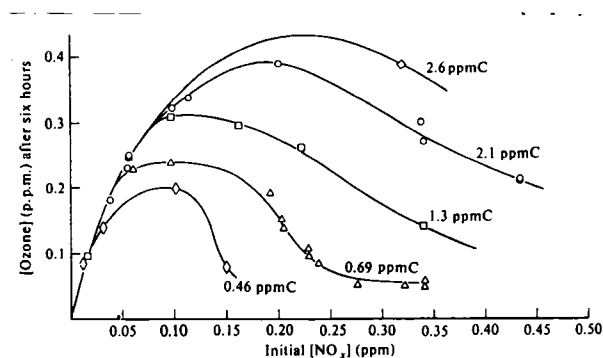
Aldehydes, which are intermediate oxidation products, and HONO are additional photochemical sources of radicals



5.8 Alkenes and PAN

Alkenes RCH=CH₂ react with OH to yield a radical RCHCH₂OH that adds O₂ to form a peroxy radical RCH(O₂)CH₂OH. As with RO₂, this radical converts NO to NO₂, and itself yields an oxy radical, RCH(O)CH₂OH that decomposes to RCHO and CH₂OH. In the atmosphere, CH₂OH reacts exclusively with O₂ to form HCHO and HO₂. Finally, reaction of HO₂ with NO regenerates the starting radical, OH.

Peroxyacetyl nitrate, PAN (ethane peroxy nitric anhydride: CH₃CO.O₂.NO₂) is formed as an adduct between NO₂ and the peroxyacetyl radical derived from CH₃CHO (see end of note 4.3). CH₃CHO is an intermediate in the oxidation of both saturated and unsaturated hydrocarbons.



5.9 Effect of altering HC/NO_x ratio

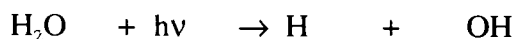
Chemistry of Atmospheres: Notes for lecture 6

6.1 Mesosphere and thermosphere

Higher energy neutral chemistry and ionic processes become important.

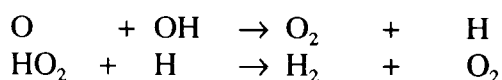
Photolysis of O₂ and gravitational separation means that O atoms begin to dominate over other neutral species (see note 1.6).

Wavelengths are short enough ($\lambda < 175\text{nm}$) to photodissociate water



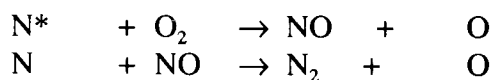
and an upward flow of H₂O must compensate.

Reactions such as

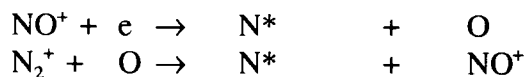


interconvert HO_x species. H atoms escape from the exosphere.

Important reactions involving NO include



N* here represents N(²D), which may be formed in processes such as



so that ion reactions affect neutral chemistry.

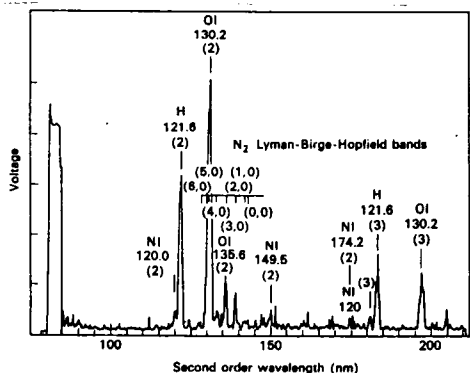
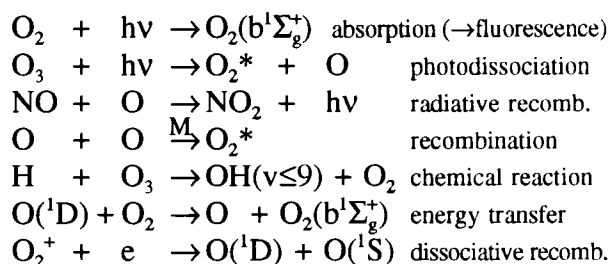
6.2 Airglow and aurora

Airglow results from the interaction of atmospheric constituents with one another and with sunlight. *Auroras* are more intense, but are mainly observed near the magnetic poles, and are excited by impact of energetic electrons and protons arriving from the Sun.

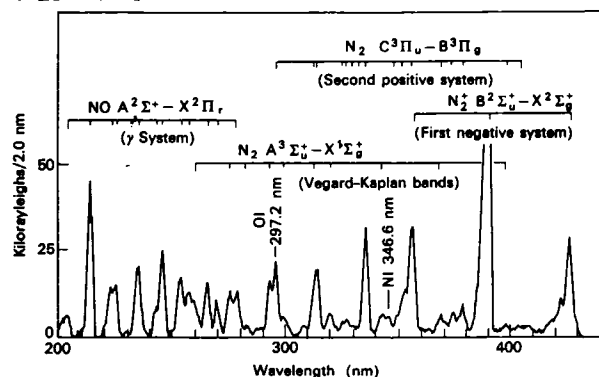
Notes 6.3 and 6.4 below reproduce parts of the UV airglow. Other very important components in the visible and near-ir include

λ/nm	Species	Name of emission
557.7	O(¹ S)	"Auroral" green line
589.3	Na(² P)	Sodium resonance line
630.0	O(¹ D)	Oxygen red line
761.9	O ₂ (b ¹ Σ_g^+)	Atmospheric band
1270	O ₂ (a ¹ Δ_g)	IR atmospheric band
2800 etc	OH ($v \leq 9$)	Meinel bands

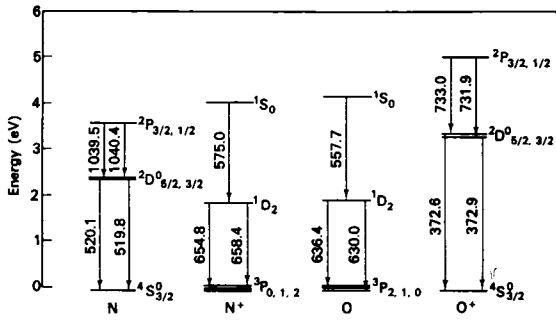
Excitation mechanisms include



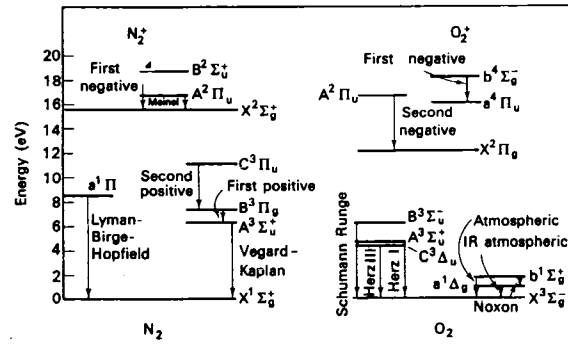
6.3 UV dayglow: 110-210nm



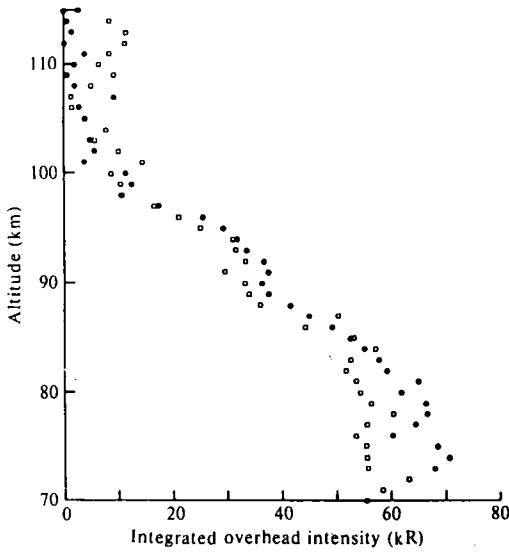
6.4 UV dayglow: 200-430nm



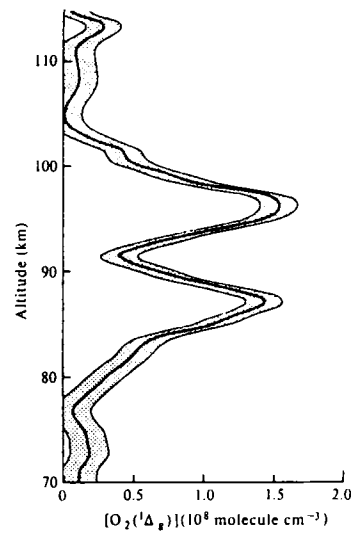
6.5 Energy levels of atoms and atomic ions (nb 1eV = 8065.7cm⁻¹ = 96.5kJ mol⁻¹)



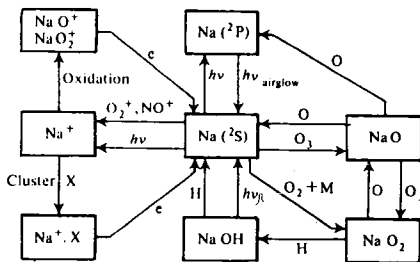
6.6 Energy levels of molecules and molecular ions



6.7 Nightglow IR atmospheric band



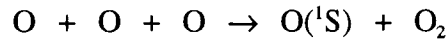
6.8 [O₂(a¹Δ_g)] derived from profile of fig. 6.7



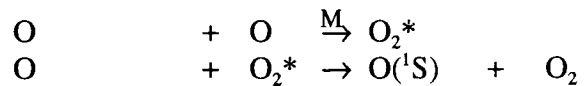
6.9 Mesospheric chemistry of sodium

6.10 Nightglow oxygen emission chemistry

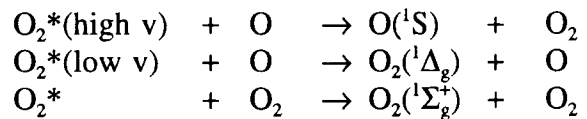
Chapman:



Barth:



Generalized scheme:



Perhaps O₂^{*} can be equated with O₂(c¹Σ_u⁻)