

Atmospheric Physics

STRATOSPHERIC MINOR CONSTITUENTS AND THE OZONE
DEPLETION PROBLEM

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Current information on the trace species in the stratosphere, the trend in the last two decades of changes in the stratospheric loading and consequences of such changes in total ozone as well as in ozone profiles are reviewed. Since anthropogenous sources must compete with natural sources, some of which may be cataclysmic (e.g., volcanoes, large solar flares), both are considered. Furthermore, there is also a possibility of solar modulation of climate through solar cycle changes in ozone. The consequences of UV variation in producing a solar cycle variation in O_3 are, therefore, also included. Since unambiguous conclusions will probably come most easily from examination of specific events, data on major events of solar flares, volcanic eruptions and nuclear explosions over the last two decades following Bauer (1978) are given.

INTRODUCTION

THE problem of ozone depletion by several manmade sources is now well known and during the last few years much work has been done in this area. However, ozone cannot be investigated in isolation and its chemistry is linked with the chemistry of many other minor constituents in the troposphere and stratosphere. These include (but are not limited to) NO , NO_2 and N_2O and HNO_3 ; Cl , ClO , HCl , CCl_4 , $CFCl_3$ and CF_2Cl_2 ; H , OH , HO_2 and H_2O and obviously O and O_2 . Since the effects depend upon the ambient stratospheric loading, the last few years have seen intense activities on: (a) experimental determination of many of the above trace constituents at stratospheric heights; and (b) laboratory measurements of the rate constants of the relevant neutral reactions.

It is a remarkable thing that the minor constituents play an important role throughout the atmosphere, although the dominant minor constituents are not the same at all heights (Fig. 1). In the mesosphere, the controlling influence of NO as a source of ionisation and consequently as a possible handle for ionospheric modification is well known. In the stratosphere, where ozone reaches its maximum concentration, we have an additional factor. At the temperature inversion trap of the stratosphere, the residence time is very long; any pollutant that strays in this region remains here for several years. Therefore, effects of manmade or natural sources like the solar flares can be cumulative at stratospheric heights. At still lower heights, the nature of the dominant minor constituents is still not clear, but aerosols must play an important role.

In the earth's atmosphere, ozone occupies a special place. It filters out some of the more lethal ultraviolet radiation from reaching the ground and has played a key role in the evolution of life on earth. In this review, I will be concerned

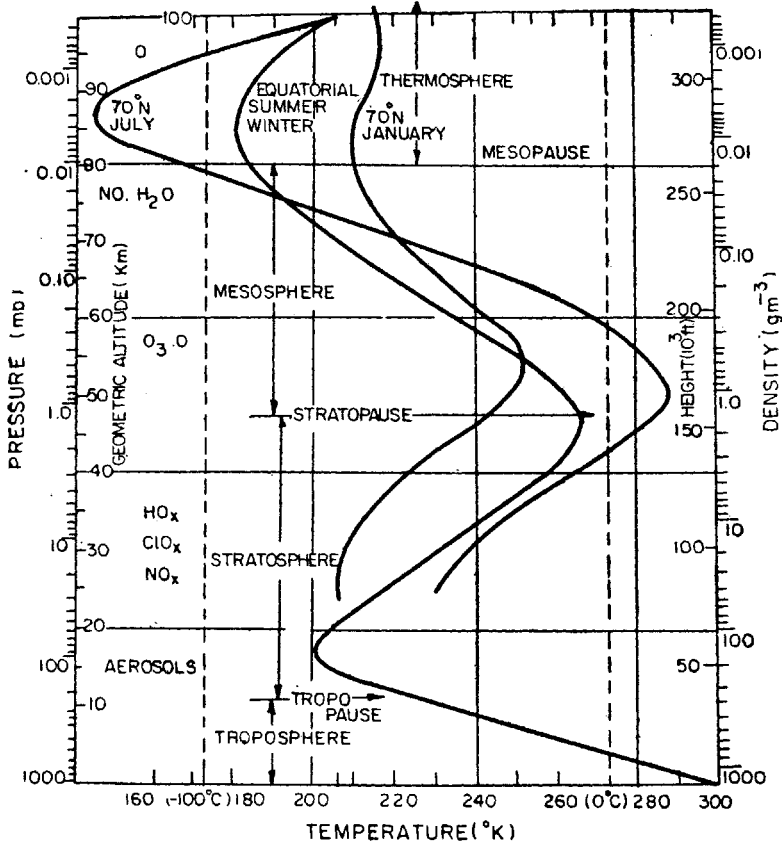


FIG. 1. Nature of the upper atmospheric medium with the temperature profiles showing the regions where the various minor constituents play important roles.

with the chemistry of this ozone, the effects of changes of different minor constituents (whether of anthropogenic origin or natural) on the distribution of stratospheric ozone, and of the possible role of ions.

In the last few years, there has been increasing concern that artificial production of nitric oxide and chlorine through a variety of manmade efforts such as supersonic aircrafts, use of industrial chlorofluoromethanes, nitrogenous fertilisers, nuclear explosions and space shuttles can substantially reduce stratospheric ozone through a complex set of reactions, some of which we have begun to understand. The effects of ozone, however, are not limited to these artificial production of nitric oxide and chlorine. Competing with these are several natural mechanisms some of which are of a cataclysmic nature. The most important amongst these are volcanic eruptions which inject a large amount of chlorine in the atmosphere and solar flares which inject a large number of particles in the atmosphere producing NO. In addition, a small, but non-negligible, solar cycle variation exists in the ultraviolet at wavelengths of interest for ozone chemistry.

One has, therefore, a complex mixture of natural and manmade modulation of the atmospheric minor constituents through a variety of sources, but primarily because of NO_x and ClO_x . The crucial parameters in a study of this kind are the reaction rates and their temperature dependence.

A related development has been a series of studies on the climatic consequences of changes in ozone. These have not been limited only to the longterm ozone depletion problem; questions on the consequences of a solar cycle variation in ozone (whatever the causes) have also been asked and results of some calculations are beginning to emerge. In this, one should examine the effects of not only changes in *total* ozone but also in the *ozone profile*; one should also compare the relative effects on climate of changes in *stratospheric* and *tropospheric* ozones.

Another approach would be to look for the consequences of individual discrete events. One might, for example, examine specific effects of : (a) atmospheric nuclear explosions for which a massive NO_x injection occurred during 1961-62; (b) volcanic eruptions, such as the Agung of 1963, for which quantitative information of injected material is available; and (c) major solar proton events of the type of August 1972.

MINOR CONSTITUENT LOADING

Increase in CO_2 , CFMs and Fertilizer Inputs in the Last Two Decades

Three major anthropogenic sources are considered here:

- (1) CO_2 concentrations (in ppmv) are those measured in Mauna Loa and South Pole and have been taken from Keeling *et al.* (1976). For Mauna Loa, values are annual average of full data after correction (59-71: 3.4%). For South Pole, values are for 1st July each year. The following points may be noted :
 - (a) Increase in concentration from 1959-71 = 3.1 per cent (South Pole) and 3.4 per cent for Mauna Loa.
 - (b) Increase is approximately 50 per cent of what would have occurred if all of the CO_2 released by burning fossil fuel and limestone had remained airborne.
 - (c) Contribution from tropical grassland fire is *much greater* than previously believed—exceeds U.S. annual emission rate. Woodburning data for Asia are:

Area subject to burning = 247×10^6 ha

[Particulates] = 11.6×10^6 tons/yr

[CO_2] = 1364×10^6 tons/yr

[CO] = 54×10^6 tons/yr

[HC] = 136×10^6 tons/yr

[NO_x] = 1.4×10^6 tons/yr

- (d) Previous belief that 90 per cent of the major pollutants originate from industries is not correct.
- (e) Direct anthropogenic production is about 7 per cent of that naturally produced.
- (f) Forest cleared for shifting cultivation (FAO, 1966) :

Far East : $8.5 \times 10^{10} \text{m}^2/\text{yr}$

Latin America : $5 \times 10^{10} - 10 \times 10^{10} \text{m}^2/\text{yr}$

Africa : Same order as above

(2) F-11 (CFCl_3) and F-12 (CF_2Cl_2) data are from Dupont (1977). Estimates for India and Argentina are: 0.0015 of Global production (F 11 + F 12).

(a) Nearly half of total production is in the USA.

(b) Note the levelling off of production around 1975.

(c) In the USA, from Dec. 5, 1978, 97 per cent of former uses of CFMs are banned.

(3) Nitrogenous fertilizer data are taken from CAST, 1976. Note that the inputs were : 3.5 MT/yr in 1950; 9.7 MT/yr in 1960; 40 MT/yr in 1974; and expected to be 200 MT/yr in 2025 A.D.

N_2O concentration is presently 329.5 ± 3.35 ppmv at ground; the tropospheric burden is 1.7×10^{15} gm and stratospheric burden is 8.17×10^{15} gm, and the estimated global flux is 210×10^{12} gm $\text{N}_2\text{O}/\text{yr}$. Increase over the last decade was 1.5 per cent (compared to 2 per cent in CO_2 over the same period).

The trend in changes in these three sources are given in Fig. 2.

Volcanoes

Volcanic eruptions are believed to be a dominant source of atmospheric gaseous chlorine (GCl). For major eruptions, the eruption cloud penetrates well into the stratosphere, in some cases right upto about 50km. Volcanic eruptions are quite common, although large eruptions are infrequent and highly variable. From the data provided by Mitchell (1970) covering a span of 120 years, it appears that a major eruption has occurred on the average of once every 3 years. The largest

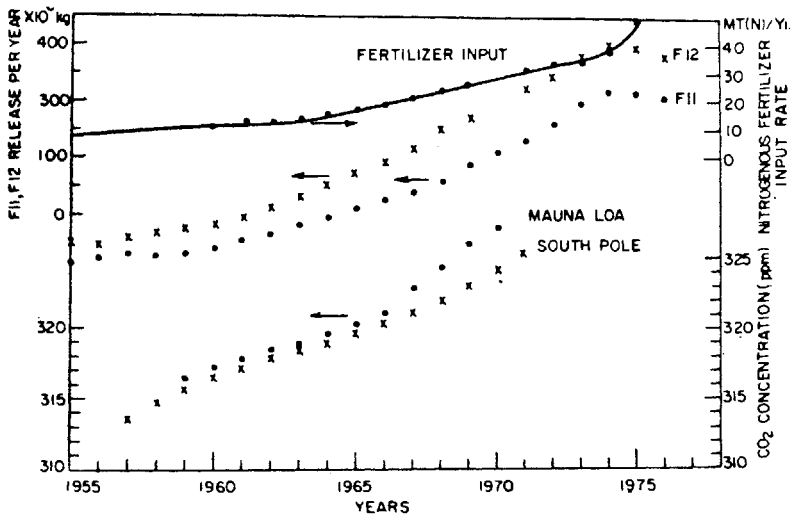


FIG. 2. Trend in the changes of three anthropogenic sources (CO_2 , CFMs and Fertilizers) in the last two decades.

eruption during this period was that of Krakatoa in 1883. The largest recent eruption was that of Mt. Agung in 1963. Other large eruptions were the Awu in 1966 and Fernandina in 1968.

The Mt. Agung volcanic eruption is of particular interest. It occurred during February 10–March 17, 1963 (8.5°S, 115.5°E), shortly after the massive injection of NO_x molecules into the stratosphere through the multimegaton nuclear test series of 1961–62. Ozone depletion due to these two different types of source (NO_x from nuclear explosion and GCl from Agung) have probably been cumulative.

A catalogue of volcanic eruptions since 1500 A.D. has been compiled by Lamb (1970); the catalogue includes about 380 eruptions. Events over the last twenty years that should be considered are as follows (Bauer, 1978) :

Major volcanic eruptions 1955–75

Date	Volcano	Latitude	Magnitude*	Max. Ht. of Injection (km)	Local Tropopause (km)
30 March '56	Bezymianny	56°N	1.4	47	9.5
21–24 May '60	Puyehue	40°S	0.2	18	11.5
17 Mar., 5 May '63	Agung	8.5°S	1.0	23	16.3
12 Nov. '64	Sheveluch	56°N	(0.3)	(25)	9.8
12 Aug. '66	AWU	3.5°N	0.1	(20)	16.5
11–12 Jun. '68	Fernandina	0.5°S	0.1	22	16.3
10–23 Oct. '74	Fuego	14.5°N	0.3	20	16

*Relative to Agung

Of special interest are the following two periods :

Quiet period : 1912–1945

Active period : 1780–1840 (24 major eruptions)

Estimated dust loading of the atmosphere due to volcanoes as compared to other sands are as follows :

- (a) Volcanoes : 4 MT in Troposphere } Average of past 20 years
 4 MT in Stratosphere }
 +
 100 MT pulse injection during volcanoes twice Krakatoa or Agung.
- (b) Particulate loading of atmosphere by human activity : 8–24 MT

Thus the two are comparable.

Of the several volcanoes, the one that offers the best scope for integrated study is the Agung. Atmospheric inputs born of Agung are :

CIX : 9×10^{33}

H₂O : 2 per cent of ambient stratospheric content

Dust : 2×10^{24} atoms of S in H₂SO₄

Minor Constituent Profiles

From the many measurements currently available based on a wide variety of techniques (with rockets, balloons and satellites, as well as groundbased), Mitra (1977) built up a reference model for minor constituents covering the entire region from surface to 100 km, thus covering the entire middle atmosphere, and not merely the stratosphere. Some modifications have since been incorporated in the 1977 model; the new model is given in Fig. 3. The main changes are the following :

- O₃ Profiles : Two profiles given—one for midlatitude by Kruger and Minzner (1976), and the other for Delhi (Kundu, 1979). For both standard deviations are also given.
- O Profile : Combines stratospheric atomic oxygen values with mesospheric values of Dickinson (1974) (daytime), mass spectrometer and 5577 nightglow (nighttime) and 1.27 μm band of O₂(1 Δ_g) at $\chi = 93^\circ$ (twilight).
- NO Profile : Combines mesospheric NO measurements by Tohmatsu and Iwagami (1975) over Trivandrum, D-region ionization requirements given by Mitra and Somayajulu (1979), lower mesospheric measurements by Hale (1977), recently published measurements by Horvath and Mason (1978) for 43–59 km and a number of stratospheric measurements.
- ClO_x Profile: Ranges indicated are results of Anderson (1979).

Profiles are generally representative of midlatitudes, but are applicable for Delhi. Indian observations are available only for O₃ and for mesospheric NO.

Aerosols

Aerosols constitute an important trace species in the troposphere and stratosphere. Profiles given here (Fig. 4) include the following :

- (1) Small (Aitken) (particles radii 0.02 μm to 0.1 μm) given by Hake *et al.* (1973) believed to be compatible with aerosol extinction coefficients measured by optical light scattering techniques (Profile 1).
- (2) Large (0.1 to 1.0 μm) particles given by Hake *et al.* (1973) (Profile 2)—range given by shades.
- (3) Small aerosol particles (0.1 μm or less) given in the U.S. Standard Atmosphere 1976—range given by shades, the shaded range based on a large number of measurements by Rosen and Hoffman (1976) using balloon-borne, light scattering counters.

Size distribution of aerosols is generally given by :

$$N(r) \propto \int r^{-v} dr,$$

where $v \sim 3$ to 4.

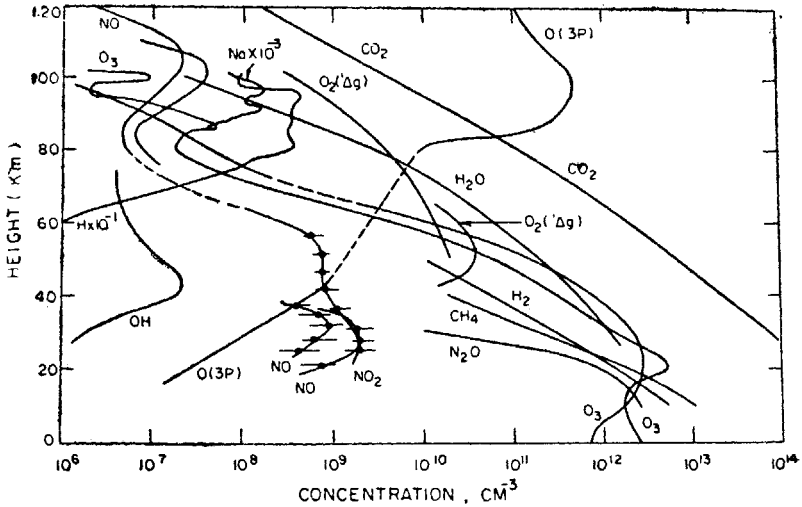


FIG. 3. Reference model for the minor constituents for the middle atmosphere.

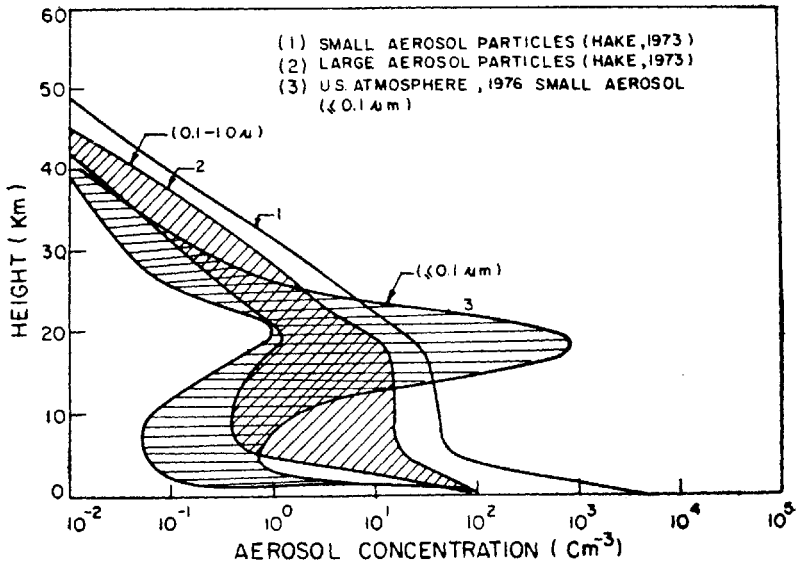


FIG. 4. Aerosol profiles for troposphere and stratosphere.

Japanese measurements (Hirono *et al.*, 1976) consistent with simultaneous lidar and small ion density measurements give:

$$n_r = C_A r^{-2.5} \text{ for } 2 \times 10^{-3} < r < 4 \times 10^{-2} \mu\text{m}$$

$$n_r = C_B r^{-4} \text{ for } 4 \times 10^{-2} < r < 3 \mu\text{m}$$

Fig. 5 gives aerosol size distributions at different heights and the difference in the distribution between the tropics and higher latitudes. The figure has been

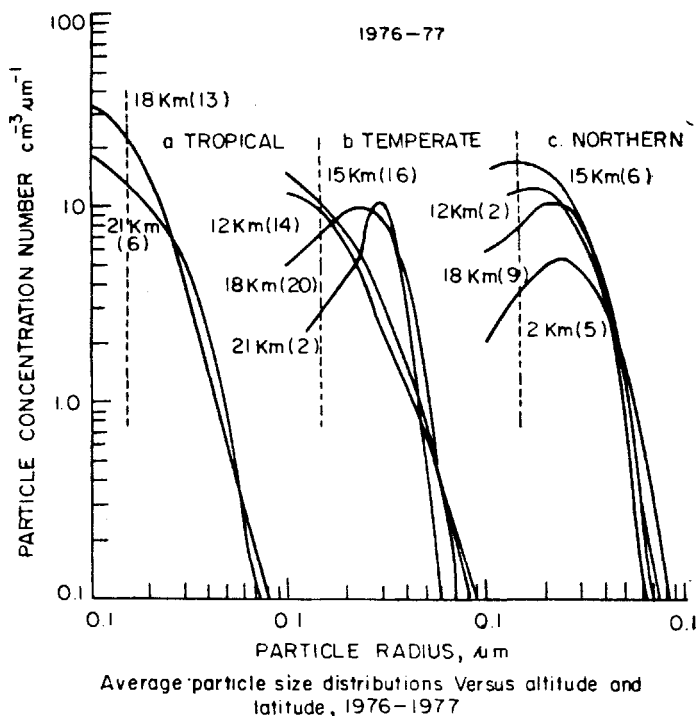


FIG. 5. Aerosol size distribution at different heights and at different latitudes (after Farlow *et al.*, 1979).

taken from Farlow *et al.* (1979). Measurements were made from tropical to northern latitudes using special collectors on a U-2 aircraft in 1976 and 1977. Particles were collected at all heights from 12 to 21 km.

Vertical dotted lines represent the threshold radius of $0.15\mu\text{m}$ for reliable measurements.

Note that while for all geographical regions, the population of *large* particles ($\gtrsim 0.3\mu\text{m}$) is nearly the same, in tropical areas there is a large increase in small particles ($r < 0.2\mu\text{m}$) which can have significant effect in small ion concentrations.

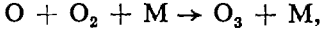
CHEMISTRY OF MINOR CONSTITUENTS

Whatever the primary sources are, the main catalytic agents from anthropogenic sources responsible for ozone changes are Cl and NO. SSTs, nuclear explosions, energetic particles (either from the sun or from galactic cosmic rays) and nitrogenous fertilizers generate NO. CFMs and volcanic eruptions generate Cl. The number of reactions involved are many. Furthermore, those involving Cl and those involving NO are not entirely independent systems. They are coupled with each other. The $\text{O}-\text{O}_2-\text{O}_3$ systems, HO_x systems, NO_x system and ClO_x constitute the basic reaction mechanism for the ambient ozone. The ClO_x system is

primarily manmade and the NO_x both manmade and natural. These and the changes in NO_x system are the ones with which we are concerned.

The reaction schemes for ozone, where all the different systems are considered, assume the form shown in Fig. 6.

The production of ozone occurs through



whereas ozone may be destroyed by atomic oxygen, hydrogen, OH, HO₂, NO or chlorine atoms.

Many of these reactions are temperature-dependent and, therefore, a knowledge of temperature at the heights concerned is a pre-requisite. Currently available information on reaction rates for important neutral reactions involving trace species is given in Table I; the table has been combined from following sources:

CIAP (1975), Mitra (1975) NBS Special Publication 513 by Hampson and Garvin (1978), NASA Reference Publication 1010 (1977), NASA Reference Publication 1026 (1978) and the JPL Bulletin (1979).

A simple picture of the effects of Cl and NO is given in Fig. 7. The basic catalytic cycle for nitric oxide involves the destruction of ozone by NO forming NO₂ and O₂. NO₂ so formed combines with atomic oxygen and reverts back to NO. The result is that ozone is converted into oxygen molecules without any change in the concentration of NO. The catalytic cycle can be repeated indefinitely resulting in destruction of large number of ozone molecules.

Chlorine acts in similar way. It is released from the destruction of chloro-fluoromethane at stratospheric heights through dissociation by solar radiation at appropriate wavelengths.

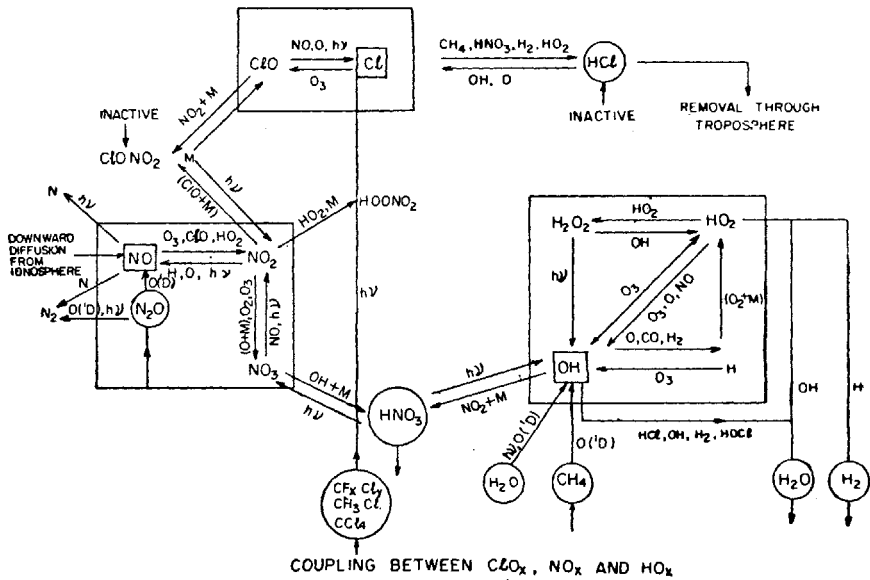


FIG. 6. Reaction scheme for ozone incorporating all the systems (ClO_x, NO_x and HO_x).

TABLE I
 Ionic reactions : reaction and suggested rate constants
 $k = a(T/300)^b e^{-c/T}$

No.	Reaction	<i>a</i>	<i>b</i>	<i>c</i>	Notes
<i>I. Dissociative Recombination :</i>					
1.	$O_2^+ + e \rightarrow O + O$	$(2.1 \pm 0.2) (-7)$ For $T_{iv} > \infty$ 100 K multiply above formula by a factor $[1 - \exp(-2677/T_{iv})]$	(-0.63 ± 0.07)	0	$T = T_e$
2.	$N_2^+ + e \rightarrow N + N$	$(1.8^{+0.4}_{-0.2}) (-7)$ For $T_{iv} > -1200$ K, multiply above formula by a factor $[1 - \exp(-3162/T_{iv})]$	(-0.39)	0	$T = T_e$
3.	$NO^+ + e \rightarrow N + O$	$(4.5 \pm 0.3) (-7)$	(-0.83)	0	} Products Uncertain
4.	$O_2^+ \cdot O_2 + e \rightarrow O + O + O_2$	$(2.0 \pm 0.5) (-6)$	(-1.0 ± 0.5)	0	
5.	$O_2^+ \cdot H_2O + e \rightarrow O + O + H_2O$	$(1.5) (-6)$	$(-0.2^{+0.2}_{-0.3})$	0	
6.	$H_3O^+ + e \rightarrow H_2O + H$ $\rightarrow H + OH$	$(1.3 \pm 0.3) (-6)$	(-0.3)	0	
7.	$H_3O^+ \cdot H_2O + e \rightarrow 2H_2O + H \rightarrow H_2 + OH + H_2O$	$(2.0 \pm 0.4) (-6)$	(-0.3)	0	
8.	$H_3O^+(H_2O)_2 + e \rightarrow 3H_2O + H \rightarrow H_2 + OH + 2H_2O$	$(5.1 \pm 0.7) (-6)$	(-0.3)	0	
9.	$H_3O^+(H_2O)_3 + e \rightarrow 4H_2O + H \rightarrow H_2 + OH + 3H_2O$	$(6.1 \pm 1.2) (-6)$	(-0.3)	0	Products uncertain
10.	$H_3O^+(H_2O)_4 + e \rightarrow 5H_2O + H \rightarrow H_2 + OH + 4H_2O$	$(7.4 \pm 1.5) (-6)$	(-0.3)	0	
11.	$H_3O^+(H_2O)_5 + e \rightarrow 6H_2O + H \rightarrow H_2 + OH + 5H_2O$	$(9.3 \pm 2.0) (-6)$	(-0.3)	0	
12.	$H_3O^+ \cdot OH + e \rightarrow H_2O + OH \rightarrow H_2 + OH + OH$	$(3) (-6)$	(-1.0 ± 0.5)	0	
13.	$O_4^+ + e \rightarrow O_2 + O_2$	$2.3(-6)$			At 205 K
14.	$CO_2^+ + e \rightarrow CO + O$	$4.0(-7)$		0	
<i>II. Mutual Neutralization :</i>					
1.	$O^+ + O^- \rightarrow O + O$	$(2.7 \pm 1.3) (-7)$	(-0.5)	0	
2.	$O_2^+ + O_2^- \rightarrow$ Products (probably $O_2 + O_2$)	$(4.2 \pm 1.3) (-7)$	(-0.5)	0	
3.	$O_3^+ + NO_2^- \rightarrow$ Products (probably $O_2 + NO_2$)	$(4.1 \pm 1.3) (-7)$	(-0.5)	0	
4.	$O_3^+ + NO_3^- \rightarrow$ Products (probably $O_2 + NO_2$)	$(1.3 \pm 0.5) (-7)$	(-0.5)	0	
5.	$NO^+ + O^- \rightarrow$ Products (probably $NO + O$)	$(4.9 \pm 1.5) (-7)$	(-0.5)	0	
6.	$NO^+ + NO_2^- \rightarrow$ Products (probably $NO + NO_2$)	$(6.4) (-7)$	(-0.5)		

(Continued)

TABLE I (Continued)

No.	Reaction	<i>a</i>	<i>b</i>	<i>c</i>	Notes
7.	$\text{NO}^+ + \text{NO}_2^- \rightarrow \text{Products}$ (probably $\text{NO} + \text{NO}_2$)	$(5.7 \pm 0.6) (-8)$	(-0.5)	0	
8.	$\text{CO}_3^-(\text{H}_2\text{O})_n$ or $\text{NO}_3^-(\text{H}_2\text{O})_n$ + $\text{H}_3\text{O}^+(\text{H}_2\text{O})_m \rightarrow \text{Products}$	$6(-8)$	(-0.5)		$n = 1, m = 3;$
9.	$\text{CClF}_2^+, \text{CClF}^+ + \text{Cl}^-$ $\rightarrow \text{Products}$	$(4.1 \pm 0.4) (-8)$	(-0.5)		
<i>III. Photodetachment :</i>					
1.	$\text{O}^- + h\nu \rightarrow \text{O} + e$	$(1.4 \pm 0.1) (0)$	0	0	These values are for normal-incidence
2.	$\text{O}_2^- + h\nu \rightarrow \text{O}_2 + e$	(0.30)	0	0	unattenuated solar flux at top of earth's atmosphere.
3.	$\text{O}_3^- + h\nu \rightarrow \text{O}_3 + e$ $\rightarrow \text{O}_2 + \text{O}^-$	(0.07) (0.27)	0 0	0	Vary with altitudes and solar zenith angles.
4.	$\text{O}_2^-\text{O}_2 + h\nu \rightarrow \text{O}_2 + \text{O}_2 + e$	(0.24)	0	0	
5.	$\text{NO}_2^- + h\nu \rightarrow \text{NO}_2 + e$	$(8) (-2 \pm 2)$	0	0	
6.	$\text{NO}_3^- + h\nu \rightarrow \text{NO}_3 + e$	$(5) (-3 \pm 2)$	0	0	
7.	$\text{OH}^- + h\nu \rightarrow \text{OH} + e$	$(1) (0 \pm 1)$	0	0	
8.	$\text{CO}_4^- + h\nu \rightarrow \text{CO}_2 + \text{O}_2 + e$	$(3) (-1 \pm 2)$	0	0	
9.	$\text{CO}_3 + h\nu \rightarrow \text{CO}_2 + \text{O}^-$	0.18	0	0	
<i>IV. Three-Body Attachment :</i>					
1.	$\text{O}_2 + e + \text{O}_2 \rightarrow \text{O}_2^- + \text{O}_2$	$(1.4 \pm 0.2) (-29)$	(-1)	600	$T = 195$ $- 600 \text{ K}$ $k_{300} = (1.9 \pm 0.3)(-30)$
2.	$\text{O}_2 + e + \text{N}_2 \rightarrow \text{O}_2^- + \text{N}_2$	$(1.0 \pm 0.5) (-31)$	0	0	
3.	$\text{O}_2 + e + \text{CO}_2 \rightarrow \text{O}_2^- + \text{CO}_2$	$(3.3 \pm 0.7) (-30)$	0	0	$T = 300$ $- 525 \text{ K}$
<i>V. Collisional Detachment :</i>					
1.	$\text{O}^- + \text{O}_2 \rightarrow \text{O} + e + \text{O}_2$	$(2.3 \pm 1.0) (-9)$	0		$26,000 \pm T_1 < 20,000 \text{ K}$ $3000 k_{300} = (1.0)(-46)$
2.	$\text{O}_2^- + \text{O} \rightarrow \text{O}_2 + e + \text{O}$	$(3.6) (-11)$	0	5000	Detailed balance calculation $k_{300} = (2.1)(-18)$
3.	$\text{O}_2^- + \text{O}_2(a^1\Delta_g)$ $\rightarrow \text{O}_2 + e + \text{O}_2$	$(2\frac{1}{2}) (-10)$	0	0	

(Continued)

TABLE I (Continued)

No.	Reaction	<i>a</i>	<i>b</i>	<i>c</i>	Notes
<i>VI. Dissociative Attachment :</i>					
1.	$O_2 + e \rightarrow O_2^- + O$	—	—	—	$k < (1)(-16)$ for $T < 2000K$ Endothermic $c > (4)(4)$ at $T < 300 K$. Strong dependence on T_v at high T_e .
2.	$O_3 + e \rightarrow O^- + O_2$	$(9 \pm 2)(-12)$	(1.5)	0	$T = 200$ — 300 K
3.	$\rightarrow O_2^- + O$	$(1.7)(-11.0 \pm 0.3)$	(1.5)	13,200	$T = T_e$. No dependence
4.	$CCl_4 + e \rightarrow \text{Products}$	4.1(-7)			dependence on T for T < 360 K
5.	$CFCI_3 + e \rightarrow \text{Products}$	1.4(-7)			$k_{300} = (1.3)$ (-30)
6.	$CF_2Cl_2 + e \rightarrow \text{Products}$	2.4(-9)			
<i>VII. Associative Detachment :</i>					
1.	$O^- + O \rightarrow O_2 + e$	$(2^{+2})(-10)$	0	0	
2.	$O^- + O_2(a^1\Delta_g) \rightarrow O_2 + e$	$(3.0^{+1.3})(-10)$	0	0	
3.	$O_2^- + O \rightarrow O_3 + e$	$(3.0^{+1.3})(-10)$	0	0	
4.	$O_3^- + O \rightarrow O_2 + O_2 + e$	$(1)(-11^{+2})$	0	0	No experi- mental data. Estimated
5.	$CO_3^- + O \rightarrow CO_2 + O_2 + e$	—	—	—	Rate is slow, compared with Reac- tion XI.11
<i>VIII. Positive-Ion Charge Transfer :</i>					
1.	$O^+ + H \rightarrow O + H^+$	$(6.8 \pm 3.0)(-10)$	0	0	
2.	$O^+ + O_2 \rightarrow O + O_2^+$	$\begin{cases} (2.0 \pm 0.2)(-11) \\ (1.3 \pm 0.2)(-12) \end{cases}$	$\begin{cases} (-0.40 \pm 0.14) \\ (1.20 \pm 0.13) \end{cases}$	0 0	$T < 1800 K$ $T > 1800 K$
3.	$O_2^+ + NO \rightarrow O_2 + NO^+$	$(6.3 \pm 2.4)(-10)$	0	0	
4.	$N_2^+ + O \rightarrow N_2 + O^+$	$(6.6)(-11 \pm 1)$	—	1945	$k_{300} = (1)$
5.	$N_2^+ + O_2 \rightarrow N_2 + O_2^+$	$\begin{cases} (5.0 \pm 1.0)(-10) \\ (2.5 \pm 0.5)(-13) \end{cases}$	$\begin{cases} (-0.8 + 0.2) \\ (1.4 \pm 0.3) \end{cases}$	0 0	$T < 3560 K$ $T > 3560 K$
6.	$H^+ + O \rightarrow H + O^+$	$(3.8 \pm 2.0)(-10)$	0	0	
7.	$OH^+ + O_2 \rightarrow OH + O_2^+$	$(2.0 \pm 0.5)(-10)$	0	0	
8.	$H_3O^+ + O_2 \rightarrow H_2O + O_2^+$	$(2.0 \pm 0.5)(-10)$	0	0	
9.	$CO^+ + O \rightarrow CO + O^+$	$(1.4 \pm 0.8)(-10)$	0	0	
10.	$CO^+ + NO \rightarrow CO + NO^+$	$(3.3 \pm 1.0)(-10)$	0	0	

(Continued)

TABLE I (Continued)

No.	Reaction	<i>a</i>	<i>b</i>	<i>c</i>	Notes
<i>IX. Positive Ion-Atom Interchange :</i>					
1.	$O^+ + N_2 \rightarrow NO^+ + N$	$\begin{cases} (1.2 \pm 0.1) (-12) \\ (8.0 \pm 2.0) (-14) \end{cases}$	$\begin{cases} (-1.0 \pm 0.4) \\ (2.0 \pm 0.2) \end{cases}$	0 0	$T < 750 \text{ K}$ $T > 750 \text{ K}$
2.	$N^+ + O_2 \rightarrow NO^+ + O$	$\begin{cases} (2.8 \pm 1.0) (-10) \\ (6 \pm 1) (-11) \end{cases}$	$\begin{cases} (0.00 \pm 0.39) \\ (0.57 \pm 0.05) \end{cases}$	0 0	$T < 4600 \text{ K}$ $T > 4600 \text{ K}$
3.	$N_2^+ + O \rightarrow NO^+ + N$	$(1.4 \pm 0.8) (-10)$	0.44	0	
4.	$O_2^+ \cdot N_2 + H_2O$ $\rightarrow O_2^+ \cdot H_2O + N_2$	$(4 \pm 2) (-9)$	0	0	
5.	$O_2^+ \cdot O_3 + O \rightarrow O_3^+ + O_3$	$(3 \pm 2) (-10)$	0	0	
6.	$O_3^+ \cdot O_2 + H_2O$ $\rightarrow O_3^+ \cdot H_2O + O_2$	$(1.5 \pm 0.5) (-9)$	0	0	
7.	$O_2^+ \cdot H_2O + O_2$ $\rightarrow O_2^+ \cdot O_2 + H_2O$	$(2) (-10)$	0	2300	$k_{300} = (9.4)$ (-14)
8.	$O_3^+ \cdot H_2O + H_2O \rightarrow H_3O^+$ $+ OH + O_2$ $\rightarrow H_3O^+ \cdot OH + O_2$	$(2.0 \pm 1.0) (-10)$ $(1.0 \pm 0.4) (-9)$	0 0	0 0	
9.	$NO^+ \cdot (H_2O)_3 + H_2O$ $\rightarrow H_3O^+ \cdot (H_2O)_2 + HNO_2$	$(7 \pm 2) (-11)$	0	0	
10.	$NO^+ \cdot CO_2 + H_2O$ $\rightarrow NO^+ \cdot H_2O + CO_2$	$(1.0 \pm 0.3) (-9)$	0	0	
11.	$H_3O^+ + H_2O$ $\rightarrow H_3O^+ + OH$	$(1.8 \pm 0.3) (-9)$	0	0	
12.	$H_3O^+ \cdot OH + H_2O$ $\rightarrow H_3O^+ \cdot H_2O + OH$	$(1.4 \pm 0.5) (-9)$	0	0	
13.	$Fe^+ + O_3 \rightarrow FeO^+ + O_3$	$(1.5 \pm 0.8) (-10)$	0	0	
14.	$S^+ + O_3 \rightarrow SO^+ + O$	$(1.6 \pm 0.3) (-11)$	0	0	
15.	$H_3O^+ \cdot (H_2O)_n + NH_3^-$ $\rightarrow NH_4^+ (H_2O)_{n-m}$ $+ (m-1) H_2O$	$2.0 (-9)$			for $n=0-4$, value varies from 1.6 to 2.6 (-9)
16.	$H_3O^+ + (H_2O)_n + CFCI_3$ $\rightarrow \text{Products}$	$4 (-10)$			for $n=0$; for $n=1, 10^{-12}$ and for $n=$ 2, 3, 10^{-13}
<i>X. Negative-Ion Charge Transfer :</i>					
1.	$O^- + O_2 \rightarrow O_3 + O_2^-$	$(5.3 \pm 2.0) (-10)$	0	0	
2.	$O^- + NO_2 \rightarrow O + NO_2^-$	$(1.2 \pm 0.4) (-9)$	0	0	
3.	$O_2^- + O_3 \rightarrow O_2 + O_3$	$(3.0 \pm 1.3) (-10)$	0	0	
4.	$O_2^- + NO_2 \rightarrow O_2 + NO_2^-$	$(8 \pm 3) (-10)$	0	0	
5.	$O_2^- + NO_3 \rightarrow O_2 + NO_3^-$	$(5) (-10)$	0	0	
6.	$O_2^- + NO_2 \rightarrow O_2 + NO_2^-$	$(2.8 \pm 1.0) (-10)$	0	0	
7.	$O_2^- + NO_3 \rightarrow O_2 + NO_3^-$	$(5) (-10)$	0	0	
8.	$NO^- + O_2 \rightarrow NO + O_2^-$	$(5 \pm 2) (-10)$	0	0	

(Continued)

TABLE I (Continued)

No.	Reaction	<i>a</i>	<i>b</i>	<i>c</i>	Notes
9.	$\text{NO}_2^- + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_3^-$	(5) (- 10)	0	0	
10.	$\text{O}_3^-\cdot\text{H}_2\text{O} + \text{O}_3 \rightarrow \text{Products}$	(3.0 ± 1.0) (- 10)	0	0	
11.	$\text{O}_2^-(\text{H}_2\text{O})_2 + \text{O}_3 \rightarrow \text{Products}$	(3.4 ± 1.0) (- 10)	0	0	
12.	$\text{H}^- + \text{NO}_2 \rightarrow \text{H} + \text{NO}_2^-$	(2.9 ± 1.0) (- 9)	0	0	
13.	$\text{OH}^- + \text{NO}_2 \rightarrow \text{OH} + \text{NO}_2^-$	(1.0 ± 0.3) (- 9)	0	0	
14.	$\text{O}_2\cdot\text{H}_2\text{O} + \text{H}_2\text{O} + \text{O}_2$ $\rightleftharpoons \text{O}_2^-(\text{H}_2\text{O})_2 + \text{O}_2$	5.4(- 28) (<i>k</i> ⁺) $1.1 \times 10^{-14}(\text{k}^{-1})$	0	0	
<i>XI. Negative Ion-Atom Interchange :</i>					
1.	$\text{O}_3^- + \text{O} \rightarrow \text{O}_2^- + \text{O}_2$	2.5(- 10)	0	0	
2.	$\text{O}_3^- + \text{NO} \rightarrow \text{NO}_2^- + \text{O}_2$	(1.0 ± 0.3) (- 11)	0	0	
3.	$\text{O}_3^- + \text{CO}_2 \rightarrow \text{CO}_3^- + \text{O}_2$	(5.5 ± 1.2) (- 10)	0	0	
4.	$\text{NO}_2^- + \text{O}_3 \rightarrow \text{O}_2 + \text{NO}_3^-$	(1.8 ± 0.6) (- 11)	0	0	
5.	$\text{NO}_3^- + \text{NO} \rightarrow \text{NO}_2^- + \text{NO}_2$	—	—	—	<i>k</i> < (1)(-12)
6.	$\text{OONO}^- + \text{NO}$ $\rightarrow \text{NO}_2^- + \text{NO}_2$	(1.5) (- 11 ± 1)	0	0	
7.	$\text{O}_2^-\cdot\text{O}_2 + \text{O} \rightarrow \text{O}_3^- + \text{O}_2$	(4 ± 2) (- 10)	0	0	$2\text{O}_2 + \text{O}^-$ may be a minor pro- duct channel.
8.	$\text{O}_2^-\cdot\text{O}_2 + \text{H}_2\text{O}$ $\rightarrow \text{O}_2^-\cdot\text{H}_2\text{O} + \text{O}_2$	(1.4 ± 0.4) (- 9)	0	0	
9.	$\text{O}_2^-\cdot\text{O}_2 + \text{CO}_2 \rightarrow \text{CO}_4^- + \text{O}_2$	(4.3 ± 1.3) (- 10)	0	0	
10.	$\text{O}_2^-\cdot\text{H}_2\text{O} + \text{CO}_2$ $\rightarrow \text{CO}_4^- + \text{H}_2\text{O}$	(5.8 ± 1.0) (- 10)	0	0	
11.	$\text{CO}_3^- + \text{O} \rightarrow \text{O}_2^- + \text{CO}_2$	(8.0 ± 2.4) (- 11)	0	0	
12.	$\text{CO}_4^- + \text{O} \rightarrow \text{CO}_3^- + \text{O}_2$	(1.5 ± 0.8) (- 10)	0	0	$\text{CO}_2 + \text{O}_3^-$ may be a minor pro- duct channel.
13.	$\text{CO}_4^- + \text{O}_2 \rightarrow \text{O}_4^- + \text{CO}_2$	(4.3) (- 10)	0	3000	$k_{300} = (2.0)$ (- 14)
14.	$\text{CO}_4^- + \text{NO}$ $\rightarrow \text{OONO}^- + \text{CO}_2$	(4.8 ± 2.0) (- 11)	0	0	
15.	$\text{CO}_3^- + \text{NO} \rightarrow \text{NO}_2^- + \text{CO}_2$	1.1(- 11)	0	0	
<i>XII. Three-Body Positive-Ion-Neutral Association :</i>					
1.	$\text{O}_2^+ + \text{O}_2 + \text{M} \rightarrow \text{O}_4^+ + \text{M}$	(2.8) (- 30)	$(- 1.0_{-1.5}^{+0.5})$	0	$T_{\text{ref}} = 307 \text{ K};$ $\text{M} = \text{O}_2.$
2.	$\text{O}_2^+ + \text{N}_2 + \text{M}$ $\rightarrow \text{O}_2^+\cdot\text{N}_2 + \text{M}$	(8 ± 4) (- 31)	$(- 1.0_{-1.5}^{+0.5})$	0	$T_{\text{ref}} = 200 \text{ K};$ $\text{M} = \text{He}.$
3.	$\text{O}_2^+ + \text{H}_2\text{O} + \text{M}$ $\rightarrow \text{O}_2^+\cdot\text{H}_2\text{O} + \text{M}$	$(1.9) \pm (- 28)$	$(- 1.0_{-1.5}^{+0.5})$	0	$T_{\text{ref}} = 296 \text{ K};$ $\text{M} = \text{O}_2.$
4.	$\text{NO}^+ + \text{N}_2 + \text{N}_2$ $\rightarrow \text{NO}^+\cdot\text{N}_2 + \text{N}_2$	(2) (- 31)	(- 4.4)	0	

(Continued)

TABLE I (Continued)

No.	Reaction	<i>a</i>	<i>b</i>	<i>c</i>	Notes
5.	$\text{NO}^+ + \text{NO} + \text{N}_2 \rightarrow \text{NO}^+\text{NO} + \text{N}_2$	(5.0) (- 30)	(- 1.0 $^{+0.5}_{-1.0}$)	0	<i>M</i> = NO
6.	$\text{NO}^+ + \text{H}_2\text{O} + \text{M} \rightarrow \text{NO}^+\text{H}_2\text{O} + \text{M}$	(1.5) (- 28)	(- 1.0 $^{+0.5}_{-1.0}$)	0	<i>M</i> = N ₂
7.	$\text{NO}^+ + \text{CO}_2 + \text{N}_2 \rightarrow \text{NO}^+\text{CO}_2 + \text{N}_2$	9.5(- 30)	(- 5 to - 6)	0	2.5(- 28) at 225 K and 9.5(- 30) at 300 K
8.	$\text{NO}^+(\text{H}_2\text{O})_2 + \text{H}_2\text{O} + \text{M} \rightarrow \text{NO}^+(\text{H}_2\text{O})_3 + \text{M}$	(1.1) (- 27)	(- 1.0 $^{+0.5}_{-1.0}$)	0	<i>M</i> = N ₂
9.	$\text{NO}^+(\text{H}_2\text{O})_2 + \text{H}_2\text{O} + \text{M} \rightarrow \text{NO}^+(\text{H}_2\text{O})_3 + \text{M}$	(1.9) (- 27)	(- 1.0 $^{+0.5}_{-1.0}$)	0	<i>M</i> = N ₂
10.	$\text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_3\text{O}^+\text{H}_2\text{O} + \text{M}$	(3.7) (- 27)	(- 1.0 $^{+0.5}_{-1.0}$)	0	<i>T</i> _{ret} = 307 K; <i>M</i> = O ₂
11.	$\text{H}_3\text{O}^+\text{H}_2\text{O} + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_3\text{O}^+(\text{H}_2\text{O})_2 + \text{M}$	(2.0) (- 27)	(- 1.0 $^{+0.5}_{-1.0}$)	0	<i>T</i> _{ret} = 307 K; <i>M</i> = O ₂
12.	$\text{H}_3\text{O}^+(\text{H}_2\text{O})_2 + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{M}$	(2.0) (- 27)	(- 1.0 $^{+0.5}_{-1.0}$)	0	<i>T</i> _{ret} = 307 K; <i>M</i> = O ₂ , N ₂
13.	$\text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_3\text{O}^+(\text{H}_2\text{O})_4 + \text{M}$	(9.0) (- 28)	(- 1.0 $^{+0.5}_{-1.0}$)	0	<i>T</i> _{ret} = 307 K; <i>M</i> = O ₂
<i>XIII. Positive-Ion Collisional Dissociation :</i>					
1.	$\text{O}_2^+\text{O}_2 + \text{M} \rightarrow \text{O}_2^+ + \text{O}_2 + \text{M}$	(2.4 ± 1.2) (- 6)	(- 1)	4900	<i>k</i> ₃₀₀ = (2.0 ± 1.0)(-13); <i>M</i> = O ₂
2.	$\text{H}_3\text{O}^+\text{H}_2\text{O} + \text{M} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{M}$	(8.8 ± 1.3) (0)	(- 1)	18,000	<i>k</i> ₃₀₀ = (7) (-26); <i>M</i> = N ₂
3.	$\text{H}_3\text{O}^+(\text{H}_2\text{O})_2 + \text{M} \rightarrow \text{H}_3\text{O}^+\text{H}_2\text{O} + \text{H}_2\text{O} + \text{M}$	(8.0 ± 3.2) (- 2)	(- 1)	11,000	<i>k</i> ₃₀₀ = (1.0 ± 0.4) (- 17); <i>M</i> = N ₂ , O ₂
4.	$\text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{M} \rightarrow \text{H}_3\text{O}^+(\text{H}_2\text{O})_2 + \text{H}_2\text{O} + \text{M}$	(5.0 $^{+5}_{-2}$; 9) (- 2)	(- 1)	8600	<i>k</i> ₃₀₀ = (2 $^{+2}_{-1}$) (-14); <i>M</i> = N ₂ , O ₂ , NO.
5.	$\text{H}_3\text{O}^+(\text{H}_2\text{O})_4 + \text{M} \rightarrow \text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{H}_2\text{O} + \text{M}$	(7.6 + 1.2) (- 1)	(- 1)	7700	<i>k</i> ₃₀₀ = (6) (- 12); <i>M</i> = O ₂

(Continued)

TABLE I (Continued)
B. O—O₂—O₃ Reactions

Reaction	Reaction Rates cm ³ /s (2 body); cm ³ /s (3 body)	Temperature K	Remarks
1	2	3	4
B.1 O(³ P) + O ₃ + M → O ₂ + M	CIAP : $6.6 \times 10^{-38} \exp(510/T)$ (M = Ar) DNA : $1.1 \times 10^{-34} \exp(510 \pm 200/T)$ (M = N ₂) JPL : $(6.2 \pm 0.8) \times 10^{-34} (T/300)^{-31 \pm 0.7}$	200–346	Rel. re-efficiencies : Ar (1.0), N ₂ (1.5), O ₃ (1.7), H ₂ O (15). (i) Major reaction of O(³ P) in the stratosphere and mesosphere. (ii) Only known source of O ₃ in the stratosphere and mesosphere.
B.2 O(³ P) + O(³ P) + M → O ₃ + M	CIAP : 4.8×10^{-33} $3.8 \times 10^{-30} T^{-1} \exp(-170/T)$ M = O ₃	298 1000 < T < 8000	B.2 Moderately important loss reaction in the upper stratosphere and mesosphere.
B.3 O(³ P) + O ₃ → 2O ₂	DNA : $3 \times 10^{-33} M = O_2$ $3 \times 10^{-33} (T/300)^{-2.0}$ M = N ₂ CIAP : $1.9 \times 10^{-11} e^{-3300/T}$ DNA : $1.5 \pm 0.3 \times 10^{-11} e^{-3340 \pm 300/T}$ JPL : $1.5 \times 10^{-11} e^{-3318 \pm 150}$	1000 200–1000	B.3 An important loss re- action for O ₃ in the upper and middle strato- sphere. Values generally agree within 2.5 per cent and believed known to a high degree of accuracy.
B.4 O(¹ D) + O ₃ → O ₂ (³ Σ _g ⁻) + O ₂ (?) (a) → O ₂ + 2O(³ P) (b)	JPL : $1.2 \times 10^{-10} (a, b)$ CIAP : $5.3 \times 10^{-10} (k_a + k_b)$ $k_a/k_b \approx 1$		

(Continued)

TABLE I (Continued)

1	2	3	4
B.5	$O(^1D) + M \rightarrow O + M$	CIAP : 4.5×10^{-11} (M = O ₂) 2.9×10^{-11} (M = N ₂) JPL : $2.9 \times 10^{-11} e^{0.7 \pm 0.50}$ (O ₂) $2.0 \times 10^{-11} e^{1.07 \pm 0.60}$ (N ₂)	
		C. HO ₂ Chemistry	
C.1	$O(^1D) + H_2O \rightarrow 2OH$	CIAP : 3.5×10^{-10} JPL : $2.3 \times 10^{-10} e^{-0 \pm 0.60}$	C.1 Major source of stratospheric HO ₂ where dissociation of H ₂ O is negligible. Rate much faster than taken in the past ($\sim 10^{-11}$).
C.2	$O(^1D) + H_2 \rightarrow OH + H$	CIAP : 2.9×10^{-10} JPL : $9.9 \times 10^{-11} \exp(-0 \pm 50)$	C.2 Another source of stratospheric HO ₂ , but smaller than C.1 by factor [H ₂]/[H ₂ O].
C.3	$O(^3P) + OH \rightarrow H + O_3$	CIAP : $(4.2 \pm 1.7) \times 10^{-11}$ DNA : $5 \pm 2 \times 10^{-11}$ JPL : $4 \times 10^{-11} e^{-0 \pm 0.300}$	
C.4	$O(^3P) + HO_2 \rightarrow OH + O_3$	CIAP : $8 \times 10^{-11} e^{-500/T}$ JPL : $3.5 \times 10^{-11} e^{-0 \pm 0.840}$	C.4 Estimate only. The actual significance of reactions C2 and C3 in the loss of O(^3P) depends on OH and HO ₂ concentrations.
C.5	$O(^3P) + H_2O_2 \rightarrow OH + HO_2$ (a)	CIAP : $2.75 \times 10^{-12} \exp(-2125/T)$	
C.6	$O(^3P) + H + M \rightarrow OH + M$	JPL : $2.8 \times 10^{-12} \exp(-2125 \pm 400/T)$ 2×10^{-32}	
C.7	$O(^3P) + OH + M \rightarrow HO_2 + M$	1.4×10^{-31}	C.6 M = Ar. C.7 CIAP gives no recommendation.

C.8	$O(^3P) + H_2 \rightarrow OH + H$			
C.9	$O_3 + H \rightarrow OH + O_2$ $\rightarrow HO_2 + O$	CIAP : $3.0 \times 10^{-14} (T) \exp(-4480/T)$ a. $(2.6 \pm 0.5) \times 10^{-11}$ b. $1.2 \times 10^{-10} \exp(-560/T)$ JPL : $1.4 \times 10^{-10} \exp(-470 \pm 200/T)$ (a)	400-2000	C.9 a. Estimated at 300 K. Probably becomes important only above 60 km. May provide major loss of O_3 in the upper mesosphere.
C.10	$O_3 + OH \rightarrow HO_2 + O_2$	CIAP : $1.6 \times 10^{-13} \exp(-1000/T)$	220-450	C.10 JPL Value: $1.6 \times 10^{-13} \exp(-940 \pm 300/T)$
C.11	$O_3 + HO_2 \rightarrow HO + 2O_2$		225-298	
C.12	$H + HO_2 \rightarrow H_2 + O_2$ $\rightarrow 2OH$ $\rightarrow H_2O + O$	JPL : $1.1 \times 10^{-14} \exp(-580 \pm 500/T)$ b. $4.2 \times 10^{-10} \exp(-950/T)$ c. $8.3 \times 10^{-11} \exp(-500/T)$ 8.3×10^{-33}	290-800 290-800 300-1000 300	C.13 $M = H_2$ $k_B/k_a = 1.3$ at 298 K.
C.13	$H + H + M \rightarrow H_2 + M$			
C.14	$H + H_2O_2 \rightarrow H_2 + HO_2$ $\rightarrow HO + H_2O$	CIAP : $(5.2 \pm 2.0) \times 10^{-12} \exp(-1400 \pm 140/T)$ 283-353	283-353	
C.15	$H + O_2 + M \rightarrow HO_2 + M$	$(5 \pm 2) \times 10^{-32} (T/300)^{-3.0 \pm 0.5}$		
C.16	$H + O_3 \rightarrow OH + O(^3P)$	$1 \times 10^{-9} \exp(-16.8/RT)$		
C.17	$H + OH \rightarrow H + O(^3P)$	$1.4 \times 10^{-14} (T) \exp(-3500/T)$		
C.18	$OH + OH \rightarrow H_2O + O(^3P)$	CIAP : $1 \times 10^{-11} \exp(-550/T)$	300-2000	C.18 For reverse reaction $O + H_2O \rightarrow HO + HO$, the rate is $1.1 \times 10^{-10} \exp(-9240/T)$
C.19	$OH + H_2O_2 \rightarrow HO_2 + H_2O$	CIAP : $1.7 \times 10^{-11} \exp(-910/T)$	300-800	C.19 JPL : $1.0 \times 10^{-11} \exp(-750 \pm 350/T)$
C.20	$OH + HO_2 \rightarrow H_2O + O_2$	CIAP : $2 \times 10^{-11} < k < 2 \times 10^{-10}$		C.20 JPL : 4×10^{-11}
C.21	$H_2 + OH \rightarrow H_2O + H$	CIAP : $3.6 \times 10^{-11} \exp(-2590/T)$	300-2500	
C.22	$HO_2 + HO_2 \rightarrow H_2O_2 + O_3$	JPL : $2.5 \times 10^{-12} \exp(-0 \pm 1246/T)$		
C.23	$OH + OH \rightarrow H_2O_2$	JPL : $2.5 \times 10^{-11} (T/300)^{-0.8}$		
C.24	$OH + H_2 \rightarrow H_2O + H$	JPL : $1.2 \times 10^{-11} \exp(-2200 \pm 200/T)$		

(Continued)

TABLE I (Continued)

1	2	3	4
D.1	$N + O_2 \rightarrow NO + O_2$	D. NO ₂ Chemistry	D.1 JPL(79) : $< 1 \times 10^{-15}$
D.2	$N + O_2 \rightarrow NO + O$	$2 \times 10^{-15} T^{-1.5} e^{-1200/T}$	D.2 Recent JPL Value is : $4.4 \times 10^{-15} \exp(-3220 \pm 340/T)$
D.3	$N + O_2(\Delta_g) \rightarrow NO + O$	$4 \times 10^{-15} < k < 4 \times 10^{-13}$	D.5 Value at (b) quoted at the IAGA symposium in Toronto (1968).
D.4	$N + O \rightarrow NO + h\nu$	2×10^{-17}	D.6 JPL(79) : 3.4×10^{-11} $\exp(-0 \pm 100/T)$
D.5	$N + O + M \rightarrow NO + M$	(a) $10^{-22}(T/300)$ (b) 9×10^{-33}	D.7 More recent values (Hute 1975) are : 3.47 $\times 10^{-12} \exp(-1533/T)$. 2.3×10^{-13}
D.6	$N + NO \rightarrow N_2 + O$	2.7×10^{-11}	D.16 JPL(79) : 1.2×10^{-13} $\exp(-2450 \pm 140/T)$
D.7	$NO + O_3 \rightarrow NO_2 + O_2$	CIAP : $9 \times 10^{-13} \exp(-1200/T)$ DNA : $9.5 \pm 1.0 \times 10^{12} \exp(-1300 \pm 100/T)$ JPL : $2.3 \times 10^{-13} \exp(-1450 \pm 200/T)$ CIAP : $2.5 \times 10^{-15} T \exp(-19500/T)$	
D.8	$NO + O \rightarrow N + O_2$	$1000-3000$	
D.9	$NO + O + M \rightarrow NO_2 + M$	$3.0 \times 10^{-33} \exp(-940/T) (M = O_2)$	$200-500$
D.10	$NO + O_2 \rightarrow NO_2 + O$	Relative M efficiencies :	
D.11	$NO + NO \rightarrow N_2O + O$	O ₂ (1.0), Ar(1.0), N ₂ (1.4)	
D.12	$NO + HO_2 \rightarrow NO_2 + OH$	9.1×10^{-13}	250-550
D.13	$NO_2 + M \rightarrow NO + O + M$	$2.2 \times 10^{-13} \exp(-32100/T)$	1200-2000
D.14	$NO_2 + O \rightarrow NO + O_2$	2×10^{-13}	300
D.15	$NO_2 + O_2 \rightarrow NO + O_3$	$1.8 \times 10^{-9} \exp(-33000/T)$	1400-2400
D.16	$NO_2 + O_3 \rightarrow NO_3 + O_2$	9.3×10^{-14}	230-550
		1.0×10^{-21}	298
		$2.8 \times 10^{-13} \exp(-25400/T)$	200-350
		DNA : $9.8 \times 10^{12} \exp(-3500 \pm 300/T)$	

D.17	$\text{NO}_3 + \text{HO} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	$3.6 \times 10^{-32} \exp(+1100/T) \text{ M} = \text{H}_6$	273-400	Recent JPL recommendation (1979) is : $(2.6 \pm 0.3) \times 10^{-30}$ $(T/300)^{-2.9 \pm 0.7}$
D.18	$\text{NO}_3 + \text{HO} + (\text{M}) \rightarrow \text{HNO}_3 + (\text{M})$	3.0×10^{-13}	220 (15 km)	
		2.2×10^{-13}	217 (20 km)	
		1.4×10^{-13}	222 (25 km)	
		8.9×10^{-13}	227 (30 km)	
		5.2×10^{-13}	235 (35 km)	
		2.6×10^{-13}	250 (40 km)	
		1.4×10^{-13}	260 (45 km)	
		$\sim 3 \times 10^{-14}$	300	
		$2.7 \times 10^{-8} \exp(-15400/T)$	800-1200	
D.19	$\text{NO}_3 + \text{HO}_2 \rightarrow \text{HNO}_3 + \text{O}_2$	$8.5 \times 10^{-14} \exp(-0 \pm 100/T)$		
D.20	$\text{HNO}_3 + \text{M} \rightarrow \text{HO} + \text{NO}_3 + \text{M}$			
D.21	$\text{HNO}_3 + \text{OH} \rightarrow \text{Products}$			
E.1	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	E. ClO_2 Chemistry	300	E.1 Other new values are : a. $2.35 \times 10^{-11} \exp(-170/T)$ b. $3.6 \pm 0.4 \times 10^{-11} \exp(-318/T)$
E.2	$\text{Cl} + \text{OCIO} \rightarrow 2\text{ClO}$	$(1.8 \pm 0.3) \times 10^{-11}$	298-588	E.2
E.3	$\text{Cl} + \text{O}_3 + \text{M} \rightarrow \text{ClOO} + \text{M}$	$2.8 \times 10^{-11} \exp(-257 \pm 100/T)$	300	E.3 Probably around 1.7×10^{-33}
E.4	$\text{Cl} + \text{ClOO} \rightarrow \text{Cl}_2 + \text{O}_2$	$5.9 \times 10^{11} \exp(0 \pm 120/T)$	298	E.5 uncertainty factor = 1.15
E.5	$\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HCl}$	$< 5.6 \times 10^{-33}$	300-696	
E.6	$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$	1.56×10^{-10}	298	
E.7	$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$	$9.9 \times 10^{-12} \exp(-1359 \pm 150/T)$		E.8 $2 \times 10^{-12} - 2 \times 10^{-10}$
E.8	$\text{Cl} + \text{HO}_2 \rightarrow \text{ClO} + \text{HO}$	$3.5 \times 10^{-11} \exp(-2290 \pm 200/T)$		E.9 k(298) = 5.0×10^{-11}
E.9	$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2(^1\Delta, ^1\Sigma)$	$1.7 \times 10^{-12} \exp(-384 \pm 400/T)$	298	E.10 k(298) = 1.8×10^{-11}
E.10	$\text{ClO} + \text{NO} \rightarrow \text{NO}_2 + \text{Cl}$	$4.5 \times 10^{-11} \exp(-0 \pm 250)$		E.11 A more recent value is $\leq 1.3 \times 10^{-18}$. The reaction is, therefore, negligible.
E.11	$\text{ClO} + \text{O}_3 \rightarrow \text{OCIO} + \text{O}_2$ $\rightarrow \text{ClOO} + \text{O}_2$	$7.7 \times 10^{-11} \exp(-130 \pm 130/T)$ $7.8 \times 10^{-12} \exp(250 \pm 100/T)$ $1 \times 10^{-12} \exp(-\geq 4000/T)$	300	

(Continued)

TABLE I (Continued)

	1	2	3	4
E.12	$\text{Cl}_2 + \text{O} \rightarrow \text{ClO} + \text{Cl}$			
E.13	$\text{HO} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$	JPL : $9.3 \pm 2.2 \times 10^{-12} \exp(-1650/T)$ $2.8 \times 10^{-12} \exp(-425/T)$	174-396 295	E.13 JPL(79) : 2.8×10^{-12} exp $(-425 \pm 100/T)$
E.14	$\text{O} + \text{OCIO} \rightarrow \text{ClO} + \text{O}_2$	$2.5 \times 10^{-11} \exp(-1166 \pm 300/T)$	298	
E.15	$\text{O} + \text{Cl}_2\text{O} \rightarrow \text{ClO} + \text{ClO}$	$1.4 \pm 0.2 \times 10^{-11}$	300	
E.16	$\text{Cl} + \text{HNO}_3 \rightarrow \text{HCl} + \text{NO}_2$			
E.17	$\text{HCl} + \text{O} \rightarrow \text{Cl} + \text{HO}$	$1.74 \pm 0.5 \times 10^{-12} \exp(-2260/T)$	296-371	
E.18	$\text{O}(\text{D}) + \text{CFCl}_3 \rightarrow \text{Products}$	5.8×10^{-10}		
E.19	$\text{O}(\text{D}) + \text{CF}_2\text{Cl}_2 \rightarrow \text{Products}$	5.3×10^{-10}		
E.20	$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$	JPL : $(1.6 \pm 0.2) \times 10^{-31} (T/300)^{-3.4 \pm 0.3}$ $(3.5 \pm 1.7) \times 10^{-32} (T/300)^{-3.8 \pm 1}$		E.20 JPL gives two recom- mendations
E.21	$\text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{ClOO} + \text{M}$	JPL : $(2 \pm 1) \times 10^{-33} (T/300)^{-1.8}$		
E.22	$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$	JPL : 3.8×10^{-12}		
E.23	$\text{CF}_2\text{Cl}_2 + \text{O}(\text{D}) \rightarrow \text{Cl} + \text{OH}$	JPL : 1.4×10^{-10}		
E.24	$\text{CFCl}_2 + \text{O}(\text{D}) \rightarrow \text{ClO} + \text{Cl} + \text{Cl}$	JPL : 2.2×10^{-10}		
F. Carbon Chemistry				
F.1	$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	JPL : $2.4 \times 10^{-12} \exp(-1710 \pm 200/T)$		
F.2	$\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$	JPL : $(2.2 \pm 1.1) \times 10^{-31} (T/300)^{-2.3 \pm 1}$		
F.3	$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$	JPL : 8×10^{-12}		
F.4	$\text{CH}_3\text{O}_2 + \text{NO}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2\text{NO}_2$	JPL : $(4.2 \pm 2.1) \times 10^{-30} (T/300)^{-3.6 \pm 2}$		
F.5	$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	JPL : 1×10^{-13}		
F.6	$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{H}_3\text{CO} + \text{HO}_2$	JPL : $5.0 \times 10^{-13} \exp(-2000 \pm 750/T)$		
F.7	$\text{OH} + \text{H}_2\text{CO} \rightarrow \text{HCO} + \text{H}_2\text{O}$	JPL : $1.7 \times 10^{-11} \exp(-100 \pm 250/T)$		
F.8	$\text{O} + \text{H}_2\text{CO} \rightarrow \text{OH} + \text{HCO}$	JPL : $2.8 \times 10^{-11} \exp(-1540 \pm 350/T)$		
F.9	$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	JPL : 5×10^{-12}		
F.10	$\text{O}(\text{D}) + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_2\text{O}$ $\rightarrow \text{OH} + \text{CH}_3$	JPL : 1.4×10^{-11} 1.3×10^{-10}		

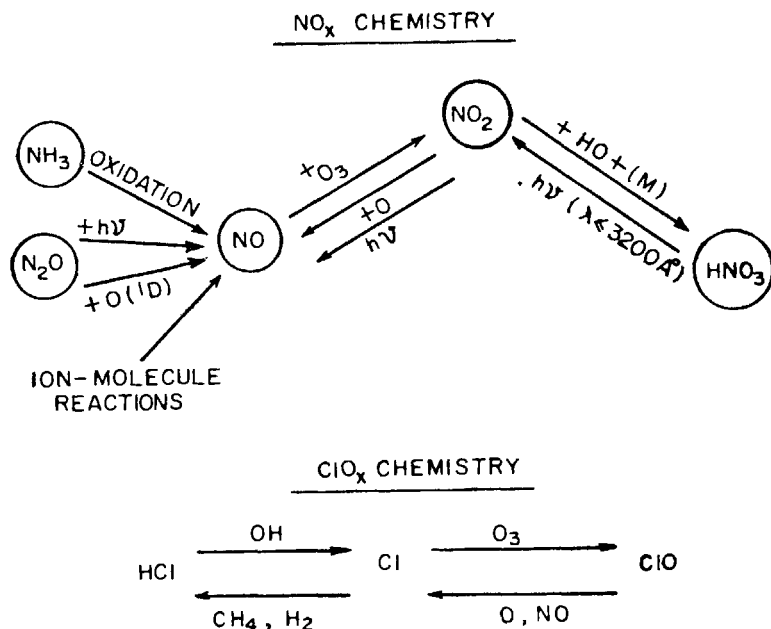
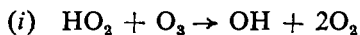


FIG. 7. Simplified scheme of NO_x and ClO_x chemistry.

Thus both chlorine and nitric oxide provide powerful ozone depleting mechanism. The relative chemical efficiencies of HO_x, NO_x, O_x and ClO_x in ozone reduction are outlined in Fig. 8, according to Crutzen and Ehalt (1977).

Several sensitivity studies have been made to see if the reactions identified and their rates are adequate. In these simultaneous studies, the primary target is to see to what extent the theoretically derived concentration profiles of trace species agree with measured profiles (such as these given in Fig. 3) for both ambient conditions or conditions of specific disturbances, such as the flare event of August 1972, for which changes of ozone are available from measurements with Nimbus satellite.

The disquieting part is that for some of the critical reactions, the reaction rates are continuously being changed. Two reactions which have changed the ozone effect *from one of depletion to one of enhancement* are the following :



The presently available rate for the first is $(1.4 \pm 0.4) \times 10^{-14} \exp(-580 \pm 100)/T \text{ cm}^3\text{s}^{-1}$ which, at stratospheric temperatures, is some 4-6 times larger than earlier values, and the current rate for the second ($= 8 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$) is nearly 40 times greater than previously adopted values. Because of reaction (i), HO_x becomes the major catalytic agent for ozone loss below 25 km; while between 25 and 40 km, NO_x dominates the ozone loss (Turco *et al.*, 1978).

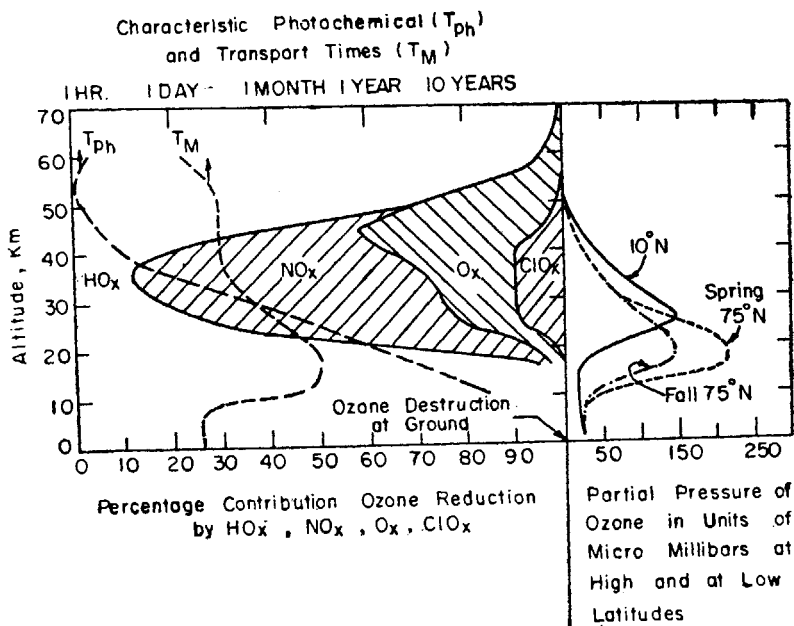


FIG. 8. Relative chemical efficiencies of HO_x , NO_x , O_3 and ClO_x in ozone depletion (after Crutzen *et al.*, 1977).

PERTURBED STRATOSPHERE

The present concern is about a stratosphere that may be changed by external means. This we call the "Perturbed Stratosphere". However, before reproducing this perturbed stratosphere (through chemical reactions), one should be able to reproduce the "ambient stratosphere". In this reproduction—it is found that in addition to the right choice of reactions and reaction rates, a right choice of eddy diffusion coefficient is involved. This must be known fairly well for different locations and for different altitudes. One should also be able to include variations across latitudes and longitudes. Often eddy diffusion information is taken from measured profiles of CH_4 .

Sensitivity studies have been carried out to test the changes that would occur if the key reaction rates are modified. One of the most important comparisons of modelling studies made was in a recent Workshop arranged at Goddard Space Flight Centre in 1977 in which the different modelling groups were first asked to present their results on the basis of their own selections of reaction rates and inputs of solar flux and perturbing sources (Hudson, 1977). Later, the Workshop decided upon a set of values for key reactions and asked the modellers to recompute ozone changes based on these values. The result was twofold :

- (i) The differences in the profiles or in $\Delta O_3/O_3$ between different models were substantially reduced.
- (ii) New values for two reactions drastically changed results.

Present estimates (steady state) with fast $\text{NO} + \text{HO}_2$ for different modelling programmes for CFMs with historical release rate upto 1975 followed by constant release rate at 1975 level are given below. Steady state release rates were assumed to be 308 kT/yr for CFCl_3 and 380 kT/yr for CF_2Cl_2 .

Lawrence Livermore Laboratory	: -15.0 p.c.
Goddard Space Flight Centre	: -13.0 p.c.
Dupont	: -12.2 p.c.
Michigan University	: -12.0 p.c.
NASA/AMES	: -16.0 p.c.
Atmospheric and Environment Research Inc.	: -10.8 p.c.
NOAA/NCAR	: -12.0 p.c.
NASA/LANGLEY	: -12.0 p.c.
AMES-2D	: -16.5 p.c.

Earlier estimates were about -7 p.c. There was thus a doubling of the effect in these calculations.

The quantitative problem of calculating ozone changes by additional injection of NO_x and ClO_x (whatever the sources) has been attempted in a number of ways. The models fall into three different categories: (a) one dimensional model in which narrow boxes are used to make up the atmosphere—the crucial parameter is the profile for the vertical eddy diffusion coefficient; (b) two dimensional models in which there is an array of eddy diffusion coefficients; small for vertical transport and large for north-south transport, involving as a minimum, three eddy diffusion parameters at each height and latitude; and (c) three dimensional models in which the equations of motions of the atmosphere are solved in a computer, although the use of eddy diffusion coefficient is not abandoned entirely.

The important point to note is that in the temperature trap of this stratosphere particles straying into this region from the troposphere tend to remain for a long time. Estimates of this stratospheric residence time have been made in a number of ways. One estimate came from the nuclear explosion series of 1961-62 for which direct samplings were made by balloons and aircrafts of excess of carbon-14, strontium-90 and other radioactive bomb materials in the atmosphere upto 33 km. The residence time was found to be of the order of a few years.

The nature of variations of different sources are discussed below :

(a) *Supersonic Aircraft and Ozone Changes*

Aircraft exhausts include NO_x and H_2O . The annual injection rate of 6.2×10^8 Kg/yr of NO_x in the Northern Hemisphere is equivalent to a fleet of 1200 Concorde-type SSTs with cruise altitudes of 17 km or approximately 600 advanced SSTs with cruise altitudes of 20 km. This also corresponds to $1000 \text{ molecules cm}^{-3}\text{s}^{-1}$ over a 1 km-thick-layer at either 17 or 20 km.

Currently, NO_x emission is estimated to be 18g/kg of fuel. In future, this is expected to be cut down to 6g/kg fuel. H_2O emission index is 1250g/kg fuel; this index will *not* be reduced with reduction of NO_x emission.

Estimated emission from all aircraft sources for 1975 (Bauer, 1978) is :

NO_2	:	4.885×10^8 kg/yr
H_2O	:	6.03×10^{10} kg/yr
CO_2	:	1.524×10^{11} kg/yr
SO_2	:	4.554×10^7 kg/yr
Particulates	:	4.554×10^6 kg/yr
Hydrocarbons	:	1.414×10^7 kg/yr
Total fuel emissions	:	4.554×10^{10} kg/yr

In estimating the effect of SSTs on the ozone profile in the stratosphere, the following scenarios have been used :

- (a) 500 SSTs;
- (b) 100 AST-100 types with cruise altitudes of 20 km and 17 km; and
- (c) varying NO_x injection rates.

Scenario C is the most reasonable since the SST types and injection rates change with time and with countries and also, once the effect of a particular injection rate is known, developmental efforts can be directed towards decreasing the effluents.

Recent estimates of ozone changes due to the above scenarios have changed greatly because of the inclusion of the new rates for reactions (i) or (ii) given above. The earlier estimate was a *reduction* by about 4.4 per cent (CIAP, 1974). The current estimates give, instead of a decrease, an increase in ozone content although ozone above 30 km continues to be significantly depleted. The magnitude of increase also depends upon whether simultaneous injection of HO_x is included or not.

Details of the new calculations (Turco *et al.*, 1978) are as follows :

- (i) Increase in total ozone by 0.15 per cent to 0.6 per cent for AST-100 type aircrafts with cruise altitudes of 20 km.
- (ii) For *case A* slightly more than 2 per cent increase for both 17 and 20 km injections (Lawrence Livermore Laboratories, 1978).

Changes in the profile are given in Fig. 9.

(b) CFMs and Ozone Changes

The industrial CFMs are frequently described by trademark names and identifying numbers such as Freon 11 for CFCl_3 and Freon 12 for CFCl_2 . The molecules CF_2Cl_2 is the most widely used of the fluorocarbons. Although production was originally confined to the USA, CFMs are now manufactured all over the world. The actual global production of CFMs during last two decades are given in Fig. 2. In recent calculations, the steady state release rate assumed is 308 KT per year

for CFCl_3 and 380 KT per year for CF_2Cl_2 . One should know that the world CFM uses grew by about 10 per cent a year through 1974; then decreased by 15 per cent in 1975.

One of the most recent calculations of the effect of CFMs on ozone has been given by Lawrence Livermore Laboratory (1978). These calculations give 15.9 per cent reduction at steady state and a reduction of 2.2 per cent *now* relative to 1950.

The height distribution of $\frac{\Delta \text{O}_3}{\text{O}_3}$ is given in Fig. 9.

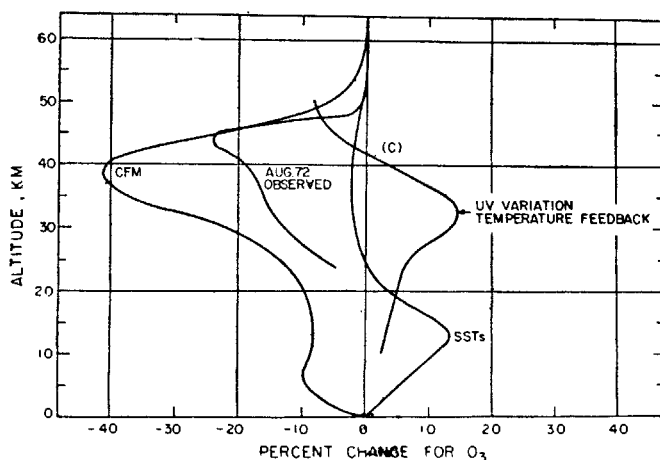


FIG. 9. Percentage change for ozone with altitude due to SST flights, CFMs, solar particle events and UV variations.

(c) Nuclear Explosion

The major source of injection of NO into the atmosphere in the past has been use of atmospheric nuclear explosions. A massive injection occurred during the Soviet and US thermonuclear explosions in the year 1961 to 1962. These tests total more than 300 MT. Subsequently, an opportunity for local observations of ozone reduction due to specific nuclear explosions came from Nimbus satellite observations of the air above French and Chinese nuclear tests. It has been pointed out that if NO_x reactions are indeed as efficient in depleting ozone as believed till recently, an examination of past ozone measurements following these nuclear explosions should provide such an evidence.

Any process which heats air above 2300 °K will produce significant quantities of NO_x as an equilibrium constituent. We would thus expect to have NO produced from the shockwaves from nuclear explosions. The following are the principal mechanisms for NO production from nuclear explosions (Bayer and Gilmore, 1975) :

- (i) Shock-heating and subsequent rapid cooling of the air
 NO production : 3.5 KT NO/MT yield

- (ii) Fireball heating of air and solar cooling by radiation, expansion and mixing in cold air
NO production : 1.5–4 KT NO/MT yield
- (iii) Bombardment of air by ionization
NO production : 0.5 KT NO/MT yield

The net yield is believed to be about 1 to 2 KT of NO per MT yield. In a recent work at Lawrence Livermore Laboratory, the nuclear explosion effects were computed with the following scenario :

- (i) Layers 9.5–16.5 km (expected stabilization altitude of 0.25 MT devices)
- (ii) 12.5–21.5 km (expected stabilization altitude of 1 MT devices)
- (iii) 17.5–28.5 km (expected stabilization altitude of 4 MT devices)

The observational effects with global total ozone values do not provide any definite evidence of any change.

(d) *Volcanic Eruption*

The details of volcanic eruption have been given in an earlier section.

The estimated total ozone changes for different volcanic eruptions and for the two special periods are given below :

- Krakatoa : -7 p.c.
 - Agung : -0.7 p.c.
 - Fuego : -0.1 p.c.
 - Augustine : - < 0.1 p.c.
 - Period 1900–1960 (quiet) : -0.3 p.c. ($\text{ClO}_x \sim 0.1$ ppbv)
 - Period 1780–1840 (active) : -3.0 p.c. ($\text{ClO}_x \sim 1$ ppbv)
- Approximately, we have :

$$1 \text{ ppbv } \text{ClO}_x \equiv -3 \text{ p.c. of } \frac{\Delta \text{O}_3}{\text{O}_3}$$

(e) *Solar Particles*

A very remarkable type of effect that must have been going on from the beginning of history is the production of NO through impact of galactic and solar cosmic ray particles as they penetrate into the mesosphere and the stratosphere. Energetic particles thrown out by the sun during solar flares is of particular concern. Solar proton events occur sporadically but are frequent (2 to 3 per month on the average) during high solar activity as compared to only a few per year during low solar activity.

The primary particles in both galactic and solar cosmic radiations are protons with a small proportion of α -particles and heavier nuclei. The energies of the particles cover 10^4 eV to over 10^9 eV and although few reach the ground, quite a few reach the stratosphere. These lead to the production of NO through ionization and dissociation of atmospheric N (see, for example, Table II).

TABLE II

Ionic reactions of interest in neutral chemistry

Direct O ₃ loss	X ⁻ + O ₃ → XO
PH → NPH	CH ₂ O, HCN, CH ₂ OH, NH ₃ , C ₂ H ₅ OH, CH ₃ CN, NaOH etc.
PH → Aerosol Clustering	Aerosols → X ⁺ [Aerosol] (Decrease in Measured Ion Concentrations)
PH + e	H/OH Production (Active Components in O ₃ Cycles)
H ₃ O ⁺ → H ₅ O ₂ ⁺	OH Production (Active Components in O ₃ Cycles) (Total 2 [OH] per Ion pair)
H ₃ O ⁺ (H ₂ O) _n + NO ₃ ⁻ (H ₂ O) _n → HNO ₃ (Inactive)	
CO ₃ ⁻ (H ₂ O) _n + H ₃ O ⁺ (H ₂ O) _n → HO _x (Active)	
GCR } SPE } → NO	No Production (Active component in O ₃ cycle) (13 NO molecules per Ion pair).

The galactic cosmic rays whose entry into the stratosphere and the mesosphere are limited to high latitudes (> 60°) has a solar cycle modulation with a quasi-period of 11 years. This produces a solar cycle modulation in ozone. The annual production of HO_x due to GCR is 7 × 10³² molecules cm⁻² and 5 × 10³² NO_x molecules cm⁻². The GCR contribution works out to be only 13 per cent at high latitudes and 6 per cent as global average.

The above, if the interpretation is valid, merely represents the normal solar cycle variation in ozone. The effect of major solar proton events, however, represents a major perturbation. August 4, 1972 flare event was the most intense event documented so far, and subsequent calculations by Reid *et al.* (1976) have been done in units of the August event. Reid and coworkers then went on to calculate the ozone depletion that would occur due to such events. Substantial depletion in ozone, must, therefore, accompany major SPEs and since the time required for the atmosphere to return to its ambient condition is about 10 years while the maximum effect occurs 1 to 2 years after the events, the effects due to different events can be cumulative.

For the August event, fortunately observation of ozone changes were made by the Nimbus-4 satellite and a comparison is possible between theory and observations. For this event, the calculated HO_x injection was 4.5 × 10³³ molecules cm⁻² and for NO_x, 3 × 10³³ molecules cm⁻²; injection altitudes were 30–35 km and the injection latitude were > 65°. The observed changes in total ozone after 19 days were a depletion by about 20 per cent at 45 km, 13 per cent at 30 km and 6 per cent at 25 km. Similar effects were observed after 8 days. Recovery was quick at heights < 1 mb (Heath *et al.*, 1977).

(f) Fertilisers

Recent calculations at Lawrence Livermore Laboratory give the following results :

- + 0.5 per cent in total ozone with doubling of N_2O
- 2.0 per cent in total ozone for $3 \times (N_2O \text{ content})$
- 5.4 per cent in total ozone for $4 \times (N_2O \text{ content})$

The NASA/Langly calculations with new rates of $HO_2 + O_3$ and $HO_2 + NO$ reaction give 2.7 per cent increase in total ozone for $1.5 \times [N_2O]$ content.

The uncertainties in the calculations are many. It is not known for example what fraction of fertiliser undergoes denitrification, how long N_2O remains in the atmosphere (usual assumption is 10 years) or the extent of contribution of the atmospheric N_2O from the oceans.

(g) *UV variation*

Heath and Thekaekura (1977) have pointed out that in the UV region responsible for ozone production there is a small but perceptible variation in the flux with solar activity. This is shown in Fig. 10. Penner and Chang (1978) have calculated the percentage deviations in total ozone as well as ozone for different height ranges as a function of solar activity using a sinusoidal 11 years cycle in EUV flux for past 47 years following curve C in Fig. 9 and current release rates of $CFCl_3$ and CF_2Cl_2 . The calculations are for 30° latitude and include all feedback mechanisms. They have then compared these theoretical solar cycle variations with plots by Angel and Korshovar (1978) of percentage deviation of ozone content. One example is given in Fig. 11.

It is seen that the theoretical curves are *not* inconsistent with observational results. Calculations give 5.1 per cent increase in total ozone from 1964 solar minimum to 1969 solar maximum and a 2.5 per cent decrease from 1970–72. The calculated changes in ozone profile are given in Fig. 11.

(h) *Solar Constant*

The most important parameter for sun-weather studies is the solar constant. A variation as small as 0.1 per cent may suffice to account for (interannual) variation of mean atmospheric temperature of the order of $0.1^\circ C$ or more. Standard solar models predict lower solar constant in the past, 75 per cent of present, 1×10^9 years ago, and a virtually constant value over short time scales ($\sim 10^7$ years). On the other hand, palaeoclimatic data suggest that the sun cannot have varied by more than 5 per cent in the last 100 million years.

Measurements of solar constants are available in a number of ways. Table III shows us a summary. Currently existing instruments can measure solar constant with absolute accuracy of 0.25 per cent and stability of 0.1 per cent. There is no positive evidence yet of a variation of solar constant of more than 0.5 per cent, although Mariner probes provided some indication of real irradiance changes of the order of 0.1 per cent on time scales of the order of 1 day to two weeks.

The recently reported drop in sun's temperature (Livingston, 1978) originally thought to indicate a change in solar constant is now believed to merely indicate a change in sun's irradiance but not in the solar constant; the change being due

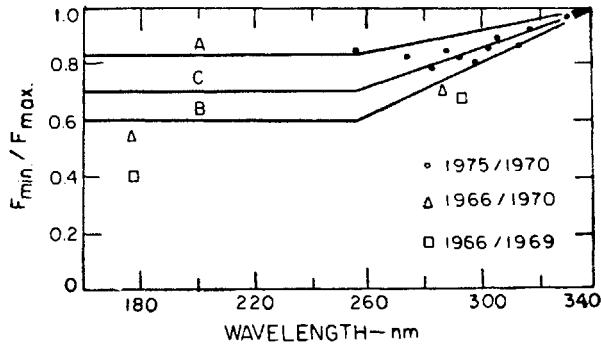


FIG. 10. Variation of solar UV-radiation with solar activity in wavelengths of interest in ozone photochemistry (after Heath & Takaekara, 1977).

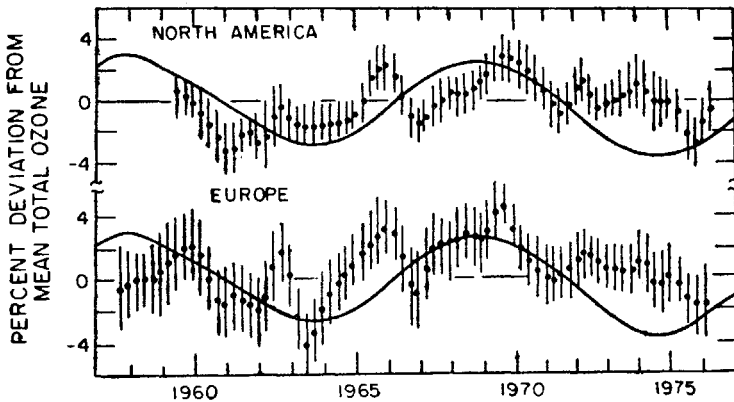


FIG. 11. Solar cycle variation of observed total ozone compared with theoretical variations based on Fig. 10 (solid lines) (after Penner & Chang, 1978).

TABLE III
Solar constant

G. W. Lockwood	Lowell observatory results from light reflected from Titan, Uranus, Neptune	Surprisingly large changes 2 ± 0.5 per cent over 1 year period
Frohlich	Critical review of measurements over last decade	$136.8 \pm 0.27 \text{ mw/cm}^2$
Wilson	JPL series of cavity radiometers—absolute accuracy believed to be $\pm 0.5 \text{ mw/cm}^2$	137.0 1968 136.6 1969
Kendall	Pacrad cavity radiometer—six aircraft observations	137.3 No detectable variation
Pacrad	Convair 990 flights—1968 35 meas. during 9 flights	137.02 ± 0.8 per cent
Livingstone		Believes 1 per cent variation due to line-blanking

to the shifting of the photon output from the blue end of the spectrum to the red or infrared due to line-blanketing.

Even if the solar constant is not very variable, solar output to the top of the atmosphere varies due to the varying distance from the sun to the earth, and changes in seasonal and latitudinal distribution of the input depending upon the variation in inclination of the earth's axis to the plane of the ecliptic and the axis of the earth's orbit.

ROLE OF IONS

In most programmes for modelling of the atmospheric minor constituents in the troposphere and the stratosphere, the possible contribution due to ions is generally ignored. This may not be so. We are outlining here some of the possible modes of contribution of ions in the minor neutral system. It is important to point out that the ionic concentrations are of the order of 10^3 cm^{-3} and this is equivalent to a neutral minor concentration of 10^6 cm^{-3} . At times when these ionization densities are greatly enhanced as during SPEs, their role becomes comparable to neutral processes, especially through ion-ion recombination processes generating active HO_x and NO_x . Ion hydration observed in the mesosphere goes through some major changes at stratospheric and tropospheric heights. Two major changes are : (i) Formation of aerosol ions both positive and negative (by attachment of proton hydrates); and (ii) a change over from a predominant $p\text{H}$ abundance above about 35 km to predominant NPH below 35 km possibly through charge exchange with specific neutral minor constituents.

Positive ion composition measurements that are currently available have been summarised in Table IV. These include both rocket and balloon measurements. Since there is a possibility that in the rocket measurements the higher order of cluster ions are dissociated, balloon measurements are preferred.

The different ways that ions can interact with minor constituents including ozone are listed in Table II. Ion chemical schemes to describe positive and negative ions at mesospheric heights exist. There are also attempts to build ion chemical schemes for stratospheric heights such as those by Ferguson (1975) and Mohnen (1975). There are also simplified approaches to include the possible effects of aerosols. Very few schemes exist, however, which consider the entire middle atmosphere as a whole. We have recently attempted to provide such a scheme by expanding our original six-ion scheme that was found to be quite effective for mesospheric heights. This is given in Fig. 12. The simplified scheme has been used sometimes in conjunction a more complex clustering sequence of positive ions given in Fig. 13, when details of ion composition in the stratosphere become the main interest. The different possibilities of $p\text{H}$ to NPH conversion are shown in this diagram. Where the exact composition of ions is not required and the interest is mainly in determining the effect of minor constituents on the ionic concentrations, as in the case of aerosols producing a localised depletion, or where only one clustering channel is believed to operate for $p\text{H}$ and NPH conversion through a minor constituent whose identity and concentration are required to be determined, or where one wishes to know the rates of production of HO_x .

TABLE IV
Positive ion composition in the stratosphere

Identification NPH	PH	Balloon (Arnold)	Rockets (Arnold)	Balloons (Arjis)	Balloon (Olsen et al.)	Identification by Ferguson
	H ⁺ (H ₂ O)		19			
Rocket			29 ± 2			
42 H ⁺ X	H ⁺ (H ₂ O) ₂		37 ± 2			41 NaOH ₂ ⁺
60 H ⁺ X(H ₂ O)	H ⁺ (H ₂ O) ₃	55 ± 1	42 ± 2 55 ± 1 60 ± 2	42 ± 3 60 ± 2		59 NaOH ₂ ⁺ H ₂ O
↑ Probably frag- mentation of H ⁺ X(H ₂ O) ₂	H ⁺ (H ₂ O) ₄	73 ± 1	By 73 ± 1 for the most abundant			
H ⁺ X(H ₂ O) ₂		78 ± 1	80 ± 2	78 ± 2 82 ± 2		77 NaOH ₂ ⁺ 2H ₂ O
						81 NaOH ₂ ⁺ NaOH
	H ⁺ (H ₂ O) ₅	91 ± 1				
H ⁺ X(H ₂ O) ₃		96 ± 1	Most abundant	96 ± 2		95 NaOH ₂ ⁺ 3H ₂ O
H ⁺ X ₂ (H ₂ O)		100 ± 1		99 ± 2		99 NaOH ₂ ⁺ NaOH.H ₂ O
	H ⁺ (H ₂ O) ₆ ?			109 ± 2(H ⁺ (H ₂ O) ₆ ?)		
H ⁺ X(H ₂ O) ₄		114 ± 2				113 NaOH ₂ ⁺ 4H ₂ O
H ⁺ X ₂ (H ₂ O) ₂		118 ± 1				117 NaOH ₂ ⁺ NaOH.2H ₂ O
H ⁺ X ₂ (H ₂ O) ₃		136 ± 2				135 NaOH ₂ ⁺ NaOH.3H ₂ O
H ⁺ X ₃ (H ₂ O)		140 ± 2				139 NaOH ₂ ⁺ 2NaOH.H ₂ C

$$\text{H}^+(\text{H}_2\text{O})_n + \text{X} \rightarrow \text{H}^+\text{X}(\text{H}_2\text{O})_{n-m} + m \text{H}_2\text{O}$$

and NO_x through the ionic reactions as an input to ozone chemistry, we believe a simplified scheme is adequate.

When aerosol effects are considered using the aerosol distribution given in Fig. 5, we get the positive ion distribution shown by the curve C in Fig. 14. We notice that a purely monotonic distribution of aerosol does not produce any observable change in the ions but an aerosol layer of the type given by the US 1976 model will produce a distinct and large ion hole that should be easy

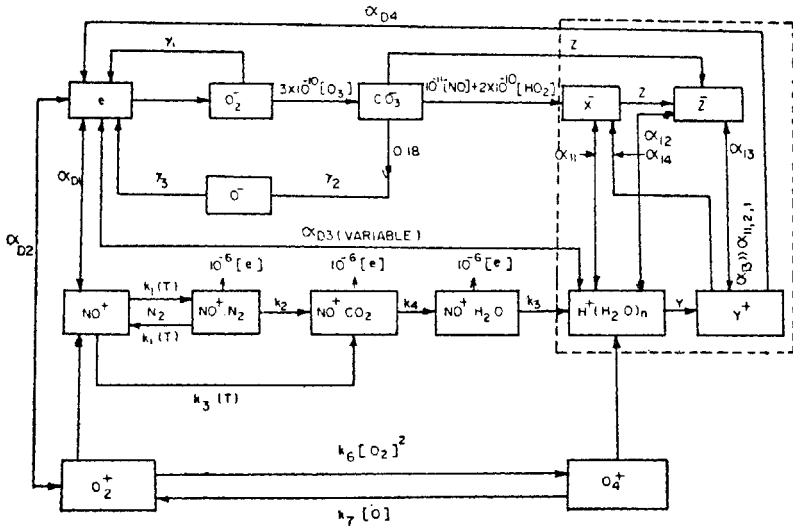


FIG. 12. Positive ion scheme for middle atmosphere as a whole.

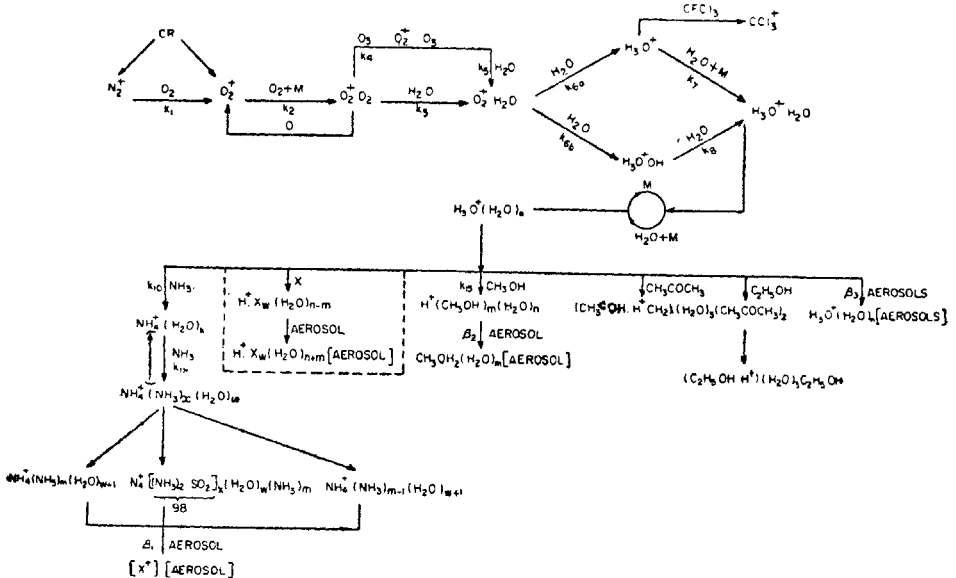


FIG. 13. Detailed scheme of positive ion sequences in stratosphere.

to measure. The scheme gives some *additional* information also. For example, from the magnitude of observed hole in N^+ , we can determine not only the concentration of aerosol particles but also that of *large* aerosol lines which should be precursors for nucleation processes.

The reactions that are likely to be important (especially during SPEs) are the 4th, 5th, 7th and 8th reactions in Table II. Dissociative recombination of proton

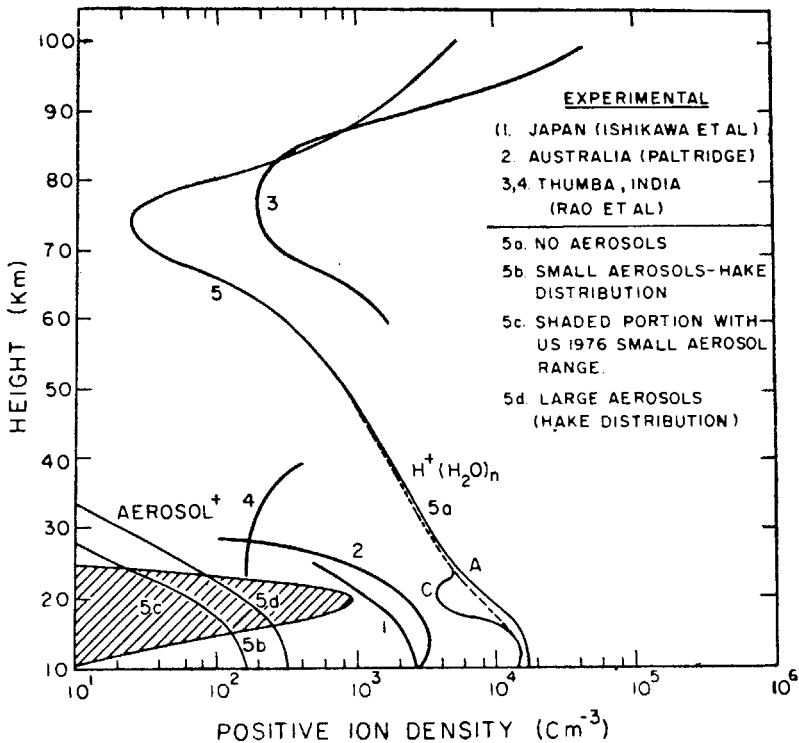


FIG. 14.⁴ Calculated changes in positive ion density with aerosols are present are shown. The calculations are made with the ionic scheme of Fig. 12 and the aerosol distributions used are those of Fig. 5.

hydrates with electrons and conversion of H_3O^+ to H_5O_2^+ produce HO_x molecules which are active components in the ozone cycle. Where N_e is not negligible, the two together generate approximately $2[\text{OH}]$ molecules per ion pair. If the ion production increases as during proton flare events or during supernova explosions we have corresponding increases in OH production rate with significant effects on ozone concentration. Thus SPEs affect the ozone chemistry not only through the production of NO (8th reaction in Table IV) and the only one considered in the interpretation of August 1972 case by Heath *et al.* (1977) but also through increased OH production through the channel $\text{O}_2^+ \rightarrow \text{H}_3\text{O}^+ \rightarrow \text{H}_5\text{O}_2^+$. Thus solar proton events should be operating in a two-fold path, only one of which has been considered in the past.

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