AERONOMIC CHEMISTRY OF OZONE

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ABSTRACT

An analysis is made of various parameters which may play a role in the atmospheric chemistry of ozone by using aeronomic equations in their general form. After considering the ozone and atomic oxygen production and destruction processes in an oxygen atmosphere, a general equation is written in which the other such production and destruction processes due to the action of hydrogen, nitrogen and halogen compounds are included.

In the mesosphere, where the atomic oxygen concentration, $n(O)$, is greater than the ozone concentration, $n(O_3)$, the transport conditions of water vapour, molecular hydrogen, and even atomic hydrogen at the upper boundary must be introduced in the equation governing the atomic oxygen concentration. Photochemical equilibrium conditions for ozone and atomic oxygen can be adopted in the lower mesosphere near the stratopause.

In the stratosphere, where $n(O_3)$ is always greater than $n(O)$, the chemical and photochemical equilibrium conditions are introduced particularly for the determination of the concentration ratios of OH and HO_2, NO and NO_2, Cl and ClO, Br and BrO. After introducing these various ratios, the equation governing ozone becomes a continuity equation which includes the transport terms of H_2O, CO, HNO_3,... The transport of water vapour is always included in the O and O_3 general equation, while the nitric acid and carbon monoxide transport terms cannot be neglected without due consideration of the lower stratosphere conditions. Furthermore, the effects of the transport terms of HNO_3, HCl annd HBr on the ratio of the OH and HO_2 concentrations and their absolute values cannot be neglected without paying attention to their numerical values in the lower stratosphere. Interchange reactions such as NO + HO_2 or NO + CH_3O_2, or disturbing terms corresponding to reactions such as ClO + OH or ClO + HO_2, must be taken into consideration in the study of the cooperative action of chemical processes and atmospheric motions in the lower stratosphere. To determine a reliable ozone distribution, the sources must be known with sufficient accuracy and the dynamical transport from the lower stratosphere to the troposphere through the tropopause (rainout, for example, at various latitudes) must be determined in association with the photochemical influence.

PREAMBLE

Sixty years ago, when Chapman (1929) was trying to explain the origin of the ozone layer by the action of the solar UV on O_2 and O_3, he had to assume that the band between 130 and 180 nm dissociates O_2 (Schumann-Runge continuum) and that the Hartley band 230-290 nm dissociates O_3. The Herzberg continuum ($\lambda < 240$ nm) had not yet been discovered and the first measurements of the absorption (Dawson et al., 1929) made at ground level between 205 and 210 nm gave a specific absorption that was tentatively attributed to molecular oxygen although no measurements of the absorption coefficients were available. Furthermore, since the ozone layer had its peak fixed in 1929 near 50 km (thin atmospheric layer, Rosseland, 1929), it was difficult (Bjerknes, 1929) to explain the first observational results obtained by Dobson (1929) showing variations in the amount of ozone associated with weather conditions (high and low pressures). The practically constant small value of the total ozone in low latitudes and the very large changes between spring and autumn in polar regions were marked and important features of these observations. Another equally interesting observational result (Chalonge and Götz, 1929) was the constancy between day and night of the total amount of atmospheric ozone.

After Götz's discovery of the Umkehreffekt he, with Dobson and Meetham were, in 1933, able to fix the peak of the ozone layer at Arosa as between 20 and 30 km. Fifty years ago in 1938 he published a general analysis of the vertical distribution of atmospheric ozone. Also in 1938, I detected in the spring at Arosa a high value of the UVB absorbed by O_3 even when its total amount was increasing. Such a result is explained by the strong amplification factor in the UV by the snow albedo associated with the multiply-scattered radiation from all directions with a perfectly blue sky at 1800 m.

Twenty five years ago, Dobson (1963), after an analysis of the data obtained during and after the International Geophysical Year, described the general characteristics of the ozone in the atmosphere. He noticed anomalies in the general world-wide pattern and particularly a major departure at Halley Bay (latitude 75°S) where the total ozone was low in the autumn and did not rise during the spring like it does near the North Pole in March. Dobson wrote : "Measurements of the upper air temperatures show that the upper part of the stratosphere at the South Pole is very cold in winter and remains cold during the spring and then suddenly, close to the time of the ozone 'jump' in November, the temperature at the highest levels rises sharply and within a few weeks may have risen 50°C. The change of temperature in the lower stratosphere is smaller and less sudden. Clearly, during November the whole structure of the south polar stratosphere has undergone a fundamental change. It seems as if in winter the south polar stratosphere is cut off from the general world-wide circulation of air by the very intense vortex of strong westerly winds which blow round the Antarctic Continent, enclosing very cold air which is rather weak in ozone; neither the ozone nor the temperature rises much until this vortex suddenly breaks down in November. However much further work will be necessary before these conditions are fully understood". Forecast or prediction !

INTRODUCTION

The ozone chemistry in the mesosphere, stratosphere and troposphere is complex because of the interactions that occur between the various trace gas constituents. Even in the atmospheric region where ozone is controlled only by photochemical processes, an over simplified analysis of the photochemistry may lead to a defective understanding of the ozone behaviour. However, since certain aspects may be neglected in a general quantitative mathematical analysis, it is essential to know not only the most important atmospheric parameters but also the basis of the photochemistry of the atmosphere. Specifically, it is essential to write the general photochemical equations and then to introduce adequate simplifications related to experimental or observational results or mathematical treatments. In this paper, an attempt is made to present the photochemical equations based on general considerations that may lead to different and various perceptions of various aspects of the ozone problem in its aeronomic viewpoint under different meteorological conditions.

The atmospheric properties of the ozone photochemistry cannot be easily understood without the use of tables representing key quantities such as, temperature, total pressure and concentrations of a standard atmosphere which can be taken as references for different types of variation. Table 1 gives numerical values which can be adopted as a reference. The various proportions of the principal constituents : $N_2 = 0.7808$ and $O_2 = 0.2095$ are given in Table 2 with ozone concentrations. This ozone distribution does not represent all conditions but can be taken as a basis to avoid unduby speculative conclusions.

In order to simplify the form of the continuity equation, with its transport term div [ ],

$$\frac{\partial n(XY)}{\partial t} + \text{div}[n(XY)w(XY)] = P(XY) - n(XY)L(XY) \tag{A}$$

where P and L denote the production and loss terms of an atmospsheric constituent XY, respectively, we shall use two symbols to represent the two members of that equation. The practice which will be followed throughout this article is to write, instead of (A), XY with angle brackets and braces

$$\langle XY \rangle = \{XY\} \tag{B}$$

Thus, $\{XY\} \equiv$ P-Ln represents the chemical contribution corresponding to the production and loss terms. When P — Ln there is photochemical or chemical equilibrium and $\langle XY \rangle$ — 0, i.e. transport processes are negligible.

No confusion can arise from the use of this last symbol, $\langle XY \rangle$, since it represents the rate of change of the number density (concentration) of the constituent XY due to transport processes. Hence, when $\partial n/\partial t = 0$, $\langle XY \rangle$ corresponds to a steady state involving the transport processes. For atoms and molecules which have short photochemical lifetimes transport does not enter and the diurnal variations can be introduced with $\{XY\} \neq 0$, since $dn(XY)/dt \neq 0$.

TABLE 1. Standard Atmosphere. Latitude 45°.

Altitude (km)	Temperature (K)	Pression (mb)	Concentration (cm^{-3})	Total (cm^{-2})
0	288	1010	$2,55 \times 10^{19}$	$2,16 \times 10^{25}$
5	256	540	1,53	1,15
10	223	265	$8,60 \times 10^{18}$	$5,66 \times 10^{24}$
15	217	121	4,05	2,59
20	217	55	1,85	1,18
25	222	25	$8,33 \times 10^{17}$	$5,47 \times 10^{23}$
30	227	12	3,83	2,57
35	237	6	1,76	1,24
40	250	3	$8,31 \times 10^{16}$	$6,19 \times 10^{22}$
45	264	1,5	4,09	3,22
50	271	0,8	2,14	1,72
55	266	0,4	1,03	$9,25 \times 10^{21}$
60	256	0,2	$6,36 \times 10^{15}$	4,87
65	239	0,1	3,47	2,48
70	220	$5,5 \times 10^{-2}$	1,82	1,20
75	200	2,9	$9,01 \times 10^{14}$	$5,40 \times 10^{20}$
80	181	1,0	4,16	2,24
85	181	$4,1 \times 10^{-1}$	1,65	$8,74 \times 10^{19}$

TABLE 2. Standard Atmosphere. Latitude 45°. N_2, O_2 with O_3.

Altitude (km)	$n(N_2)$ (cm^{-3})	$N(N_2)$ (cm^{-2})	$n(O_2)$ (cm^{-3})	$N(O_2)$ (cm^{-2})	$n(O_3)$ (cm^{-3})	$N(O_3)$ (cm^{-2})
0	$1,99 \times 10^{19}$	$1,68 \times 10^{25}$	$5,34 \times 10^{18}$	$4,50 \times 10^{24}$	$8,00 \times 10^{11}$	$9,35 \times 10^{18}$
5	1,20	$8,96 \times 10^{24}$	3,21	2,40	5,67	9,01
10	$6,71 \times 10^{18}$	4,40	1,80	1,18	$1,13 \times 10^{12}$	8,67
15	3,16	2,01	$8,48 \times 10^{17}$	$5,41 \times 10^{23}$	2,57	7,66
20	1,44	$9,21 \times 10^{23}$	3,87	2,47	4,77	5,80
25	$6,50 \times 10^{17}$	4,25	1,75	1,14	4,32	3,45
30	2,99	2,00	$8,02 \times 10^{16}$	$5,37 \times 10^{22}$	2,52	1,73
35	1,37	$9,61 \times 10^{22}$	3,69	2,58	1,40	$7,65 \times 10^{17}$
40	$6,49 \times 10^{16}$	4,81	1,74	1,29	$6,07 \times 10^{11}$	2,78
45	3,19	2,30	$8,56 \times 10^{15}$	$6,71 \times 10^{21}$	2,03	$9,08 \times 10^{16}$
50	1,67	1,34	4,47	3,60	$6,61 \times 10^{10}$	2,95
55	$9,10 \times 10^{15}$	$7,22 \times 10^{21}$	2,44	1,94	2,15	$9,58 \times 10^{15}$
60	4,97	3,80	1,33	1,02	$7,00 \times 10^{7}$	3,09
65	2,71	1,94	$7,26 \times 10^{14}$	$5,20 \times 10^{20}$	2,21	$9,98 \times 10^{14}$
70	1,42	$9,35 \times 10^{20}$	3,81	2,51	$7,00 \times 10^{6}$	3,38
75	7,04	4,21	1,89	1,13	$(2,21 \times 10^{6})$	1,29
80	3,25	1,74	$8,71 \times 10^{13}$	$4,64 \times 10^{19}$	$(7,00 \times 10^{7})$	$6,34 \times 10^{13}$
85	1,29	$6,78 \times 10^{19}$	3,46	1,79	$(5,25 \times 10^{5})$	3,28

As an example, atomic oxygen is described by $\partial n(O)/\partial t + \text{div}[n(O)w(O)] = P - Ln(O)$ or $\text{div}[n(O)w(O)] = P - Ln(O)$ which is represented by symbol $<O>$, and $dn(O)/dt = P - Ln(O)$ with $\text{div}[n(O)w(O)] = 0$, by $\{O\}$, and $dn(O)/dt = P - Ln(O) = 0$ by $\{O\} = 0$.

PURE OXYGEN ATMOSPHERE

In order to introduce the aeronomic problem in its specific aspects, it is useful to begin the analysis with the study of the photodissociation of molecular oxygen, and its subsequent reactions, in an oxygen atmosphere without any active chemical action on the part of other constituents.

Radiation of wavelengths less than 242 nm absorbed by molecular oxygen O_2 causes its photodissociation into oxygen atoms :

$$(J_2); \quad O_2 + h\nu(\lambda < 242 \text{ nm}) \rightarrow 2\,O \tag{1}$$

The principal photodissociation process in the Schumann-Runge continuum ($\lambda < 175$ nm) occurs in the thermosphere

$$O_2 + h\nu(\lambda < 175 \text{ nm}) \rightarrow O(^3P) + O(^1D) \tag{1a}$$

All oxygen atoms produced by this process are transported downward below 100 km where they recombine above the tropopause. The basic aeronomic parameter is therefore the total production of oxygen atoms. Since a variation with solar activity, less than a factor of 2, must occur, an appropriate value for the atomic oxygen production rate is of the order of $(2 \pm 0.5) \times 10^{12}$ atoms $\text{cm}^{-2}\,\text{s}^{-1}$. The total thermospheric production of oxygen atoms fix the atomic oxygen concentrations near the mesopause and their variations with solar activity and latitude.

In the mesosphere and stratosphere, three spectral ranges affect the O_2 absorption; namely, Lyman-α at 121.6 nm, only in the mesosphere, the Schumann- Runge band system ($\lambda < 200$ nm) in the mesosphere and partly in the stratosphere where the Herzberg continuum between 242-200 nm plays a leading role which is controlled by the ozone absorption in its Hartley band. The peak of the O_2 photodissociation occurs in stratosphere (near 35 km for an overhead sun) where the total number of O_2 molecules photodissociated is of the order of 10^7 cm^{-3} sec^{-1}. Below the ozone peak (< 25 km) the photodissociation rate decreases rapidly, particularly when the solar zenith angle increases. At 20 km there is a difference of a factor of 100 between 0° and 60°.

In the case of Lyman-alpha, it is necessary to take into account the variation with wavelength of the O_2 absorption cross-section and of the profile of the solar line, simultaneously. The effective optical depth increases from 0.1 to 10 as the total numbebr of O_2 absorbing molecules increases from 10^{19} to 10^{21} cm^{-2} i.e. from the mesopause to 60 km for an overhead sun (see table 2) and from the thermosphere to 70 km for a solar zenith angle of about 70°. A detailed computation shows that Lyman-alpha plays a role in the photodissociation of O_2 in the upper mesosphere which may increase the total photodissociation by about 25% when $N(O_2) = 10^{20}$ cm^{-2} and solar conditions are relatively quiet.

Above the mesopause, the photodissociation frequency of O_2 is of the order of 10^{-7} s^{-1} for the Schumann-Runge bands and about 5 x 10^{-10} s^{-1} for the Herzberg continuum.

The addition of the photodissociation produced in the Herzberg continuum increases the total photodissociation at 95 km by 1-2% and at 90 km by 2-4%.

At the mesopause, the contribution to the total photodissociation of O_2 by the Herzberg continuum increases from 3% for sec χ = 1 and $N(O_2)$ = 1.8 x 10^{19} cm^{-2} to 9% for sec χ = 4 and $N(O_2)$ = 7.1 x 10^{19} cm^{-2}.

In the 60-65 km region, the role of the Herzberg continuum in the total production of atomic oxygen increases up to more than 50% when $N(O_2)$ = 2 x 10^{21} cm^{-2}.

A detailed calculation at 60 km from an overhead sun to a solar zenith angle of 70° corresponding to $N(O_2)$ = 1 x 10^{21} cm^{-2} - 4 x 10^{21} cm^2 shows that $J(O_2)$ decreases from 1.5 x 10^{-9} to 8.2 x 10^{-10} s^{-1} with an increasing relative role of the Herzberg continuum from about 40% to 65%. Consequently, the atomic oxygen production lies between 4 and 2 x 10^6 atoms cm^{-3} s^{-1} for solar zenith angles between 0° and 70°.

The effect of the O_3 absorption on the transmittance, and therefore on $J(O_2)_{SRB}$ is negligible or relatively small in the mesosphere. From 60 to 50 km, ozone decreases the photodissociation frequency, 10^{-10} s^{-1} < $J(O_2)_{SRB}$ < 10^{-9} s^{-1}, from 0.02 x 10^{-10} s^{-1} to 0.04 x 10^{-10} s^{-1}, respectively, i.e. less than 4%. Thus, the adoption of a general formula from the mesopause to the stratopause can be envisaged for $J(O_2)_{SRB}$. The result is

$$J(O_2)_{SRB} = 6.55 \times 10^6 N^{-0.7567} \text{ s}^{-1}$$

for

$$5 \times 10^{18} \leq N(O_2) \leq 1 \times 10^{22} \text{ cm}^{-2}$$

i.e. up to 95 and down to 50 km near N = 10^{22} cm^{-2}, with an accuracy generally better than $\pm$ 5% and always better than $\pm$ 10%. Such a result corresponds to

$$5 \times 10^{-8} \geq J(O_2)_{SRB} \geq 5 \times 10^{-10} \text{ s}^{-1}.$$

Nevertheless, the accuracy in the solar spectral irradiance values and their variations with solar activity should be improved.

In the stratosphere, the absorption in the 202-242 nm wavelength range by O_2 of the Herzbberg continuum is the direct dominant source of odd oxygen and is at the same time a source of the atmospheric opacity. However, the O_3 absorption contributes greatly to the diminution of the atmospheric transmittance. The atmospheric absorption of O_3 must be taken into account between 50 and 60 km (Table 2). For an overhead sun, the O_2 photodissociation frequency decreases by about 10% when the ozone effect is included at the stratopause. Thus, at 55 km for example, where the photodissociate rate of O_2 is about 2 x 10^6 molecules cm^{-3} s^{-1} for solar zenith angles between 0° and 75° and the ozone concentration is of the order of 2 x 10^{10} molecules cm^{-3}, the photochemical equilibrium conditions should correspond to 5 x 10^3 - 10^4 s.

In any case, there is an isophotolytic level at stratospheric levels for any adopted values of the O_2 cross-sections; it corresponds to an O_2 photodissociation frequency of the order of 5×10^{-12} s^{-1} at various altitudes between 25 km and 35 km related to the zenith angle. At these altitudes the effect of ozone on the atmospheric opacity is never less than 50% and reaches between 70% and 90%. Thus, particular attention should be given to the determination of the absolute accuracy of the absorption cross-sections of O_2 and O_3 in the 202-222 nm spectral region coinciding with the wavelength interval which plays a major role for the photodissociation of oxygen in the lower stratosphere. Below 20 km to the tropopause level the photodissociation rates of O_2 are very small and the photoproduction of oxygen atoms may be negligible compared with that of other indirect processes.

Thus, there is a large difference in the total annual production of oxygen atoms with latitude. At the equator, the photoproduction is not less than 10^{18} atoms cm^{-2} day^{-1} practically constant during the year. At 45°, there is a strong variation of about a factor of 5 between summer and winter. At latitudes greater than 60°, the winter production is negligible. Furthermore, the tropical regions ($\pm$ 30°), the mean latitude regions (45 $\pm$ 15°) and the polar regions (60-90°), which correspond to about 50, 40 and 10% of the earth's surface, indicate a direct association between the seasonal and latitudinal distribution of the atomic oxygen production and therefore of the stratospheric production of O_3. Finally, the variation with the earth-to-sun distance of the solar irradiance between the first week of January and the first week of July is about 6.6%. Thus, the ozone production at noon at 23° S in summer (January) is about 7% greater than its production at 23°N in summer (July).

Ozone photodissociation occurs because of its absorption of solar radiation in the visible and the ultraviolet,

$$(J_3); \quad O_3 + h\nu(\lambda < 1m\mu) \rightarrow O_2 + O \tag{2a}$$

But at $\lambda < 310$ nm, the O_3 photodissociation leads to $O(^1D)$ with an average quantum yield between 1 and 0.9

$$(J_3^*); \quad O_3 + h\nu(\lambda < 307 \text{ nm} \rightarrow O_2(^1\Delta_g) + O(^1D) \tag{2b}$$
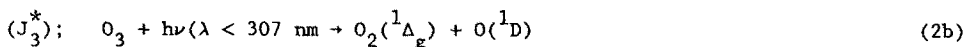
and the excited oxygen atom $O(^1D) \equiv O^*$ can react with atmospheric constituents even if quenching effect of O_2 and N_2 is important ,

$$(k_M^*); \quad O^* + N_2 \text{ or } O_2 = (4.3 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \tag{3}$$
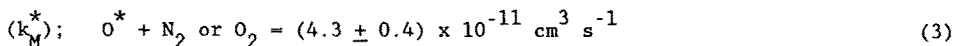
In addition to the important Hartley band absorption, O_3 also absorbs at $\lambda < 310$ nm (Huggins bands) and in the visible (Chappuis bands).

The photodissociation frequency, even at ground level, in the Chappuis bands is of the order of

$$J_3(\text{Chappuis}) = 3 \times 10^{-4} \text{ s}^{-1} \tag{2c}$$

without any multiple scattering and albedo effect. In the spectral region of wavelengths greater than 310 nm (Huggins bands) the $O(^1D)$ production decreases with wavelength and

temperature to reach a quantum yield of less than 0.1 at 325 nm. The effect of the tail in the I^* production is important in the troposphere; it varies with the temperature and the solar zenith angle and is influenced by multiple scattering and the albedo. Thus, the chemical action of O^* will depend on latitude and season as well as on the effect of the ozone content and its variation.

Finally, the O_3 photodissociation corresponds to the total photodissociation coefficients J_3 of the order of 10^{-2} s^{-1} in the mesosphere and to not less than 3×10^{-4} s^{-1} in the stratosphere. Since the O_3 photodissociation rate is greater than 10^8 cm^{-3} s^{-1} in the stratosphere (below 40 km), $n(O_3)J_3 > n(O_2)J_2$.

The recombination of atomic oxygen in the presence of a third body (N_2, O_2)

$$(k_1); \quad O + O + M \rightarrow O_2 + M \tag{4}$$

with

$$k_{1M} = 4.7 \times 10^{-33}(300/T)^2 \, n(M) \, cm^3 \, s^{-1}$$

must be considered in the mesosphere above 70 km, but plays no practical role in the study of stratospheric processes. The reaction which is significant at all altitudes is the association of oxygen atoms with oxygen molecules

$$(k_2); \quad O + O_2 + M \rightarrow O_3 + M \tag{5}$$

with

$$k_{2M} = 6 \times 10^{-34}(300/T)^{2.3} \, n(M) \, cm^3 \, s^{-1} \tag{5a}$$

which leads to the formation of ozone.

Finally, ozone molecules and oxygen atoms react together

$$(k_3); \quad O + O_3 \rightarrow 2O_2 \tag{6}$$

with

$$k_3 = 8.0 \times 10^{-12} \, e^{-2060/T} \, cm^3 \, s^{-1} \tag{6a}$$

and lead to the re-formation of oxygen molecules and the destruction of ozone.

The equations governing the rate of change of the concentrations of ozone, $n(O_3)$, and of atomic oxygen, $n(O)$, are therefore

$$<O> + 2k_1 n(M) n^2(O) + k_2 n(M) n(O_2) n(O) + k_3 n(O_3)(O) = 2n(O_2)J_2 + n(O_3)J_3 \tag{7}$$

and

$$<O_3> + n(O_3)J_3) + k_3 n(O) n(O_3) = k_2 n(M) n(O_2) n(O) \tag{8}$$

Since the life-time of an oxygen atom r_0 varies (equation 5 and Table 2) from about 10 s to about 10^5 s at 85 km, it is evident that, above a certain altitude in the mesosphere $n(O) > n(O_3)$, and also that O_3 is in photochemical equilibrium in the solar radiation field. The equations (7) and (8) lead, in the upper mesosphere, to

$$<O> + 2k_{1M} n^2(O) + 2k_3 n(O_3) n(O) = 2 \, n(O_2)J_2 \tag{9}$$

with the equilibrium value of $n(O_3) = n_*(O_3)$

$$n_*(O_3)/n(O) = k_2 n(M) n(O_2)/(J_3 + k_3 n(O)) \tag{10}$$

It is also evident that, in the middle mesosphere (< 70 km), there is a region where photochemical equilibrium prevail, and (9) becomes

$$k_{1M} n^2(O) + k_3 n(O_3) n(O) = n(O_2) J_2 \tag{11}$$

which yields

$$n_*^2(O) = n(O_2) J_2/k_{1M} \left(\frac{1 + k_2 k_3 n(O_2)}{k_1 J_3} \right) \tag{12}$$

with

$$n_*(O_3)/n_*(O) = k_2 n(M) n(O_2)/J_2 \tag{13}$$

if $J_3 > k_3 n(O)$.

In the stratosphere, $n(O) < n(O_3)$ and atomic oxygen is always in photoequilibrium in the solar radiation field. Instead of (9), the general equation becomes

$$<O_3> + 2k_3 n(O) n(O_3) = 2n(O_2) J_2 \tag{14}$$

Since

$$n_*(O) = \frac{n(O_3) J_3 + 2n(O_2) J_2}{k_2 n(M) n(O_2) + k_3 n(O_3)} \tag{15}$$

the rate of change of $n(O_3)$ in a pure oxygen atmosphere becomes

$$<O_3> + 2n^2(O_3) \frac{J_3 k_3}{k_2 n(M) n(O_2 + k_3 n(O_3)} = 2n(O_2) J_2 \frac{k_2 n(M) n(O_2) - k_3 n(O_3)}{k_2 n(M) n(O_2) + k_3 n(O_3)} \tag{16}$$

It can be shown that, under atmospheric conditions,

$$k_3 n(O_3) < k_2 n(M) n(O_3) \tag{17}$$

and is always correct in the stratosphere since the limiting value $n_1(O_3)$, which depends on the number of oxygen atoms available

$$n_1(O_3) = k_2 n(M) n(O_2)/k_3, \tag{18}$$

can never be reached. The practical equation is, therefore, with (16) and (17),

$$<O_3> + 2n^2(O_3) \frac{k_3 J_3}{k_2 n(M) n(O_2)} = 2n(O_2) J_2 \tag{19}$$

which is the standard form of the ozone equation used in a pure oxygen stratosphere.

At the stratopause level and in its neighbourhood (± 10 km) photochemical equilibrium conditions apply, and the ozone concentration $n_*(O_3)$ is

$$n_*(O_3) = \frac{n(O_2)J_2}{n(O_3)J_3 + n(O_2)J_2} \; n(M)n(O_2) \; \frac{k_2}{k_3} \tag{20}$$

with

$$n_*(O) = \frac{n(O_3)J_3 + n(O_2)J_2}{k_2 n(M)n(O_2)} \tag{21}$$

Below the stratopause, application of the atmospheric condition

$$n(O_3)J_3 \gg n(O_2)J_2 \tag{22}$$

to (20) and (21) gives

$$n_*^2(O_3) = \frac{J_2}{J_3} \; n(M)n^2(O_2) \; \frac{k_2}{k_3} \tag{23}$$

$$n_*(O) = \frac{n(O_3)J_3}{k_2 n(M)n(O_2)} \tag{24}$$

and

$$\frac{n^*(O_3)}{n^*(O)} = \frac{k_2 n(M) \; n(O_2)}{J_3} \tag{25}$$

These equations are the photochemical equilibrium equations of ozone and atomic oxygen in an oxygen atmosphere where other constituents play no chemical role. With a numerical value $n(O_3) = 7 \times 10^9$ cm^{-3} at 60 km and the reaction coefficients adopted here, the photodissociation frequency of O_3 would be of the order of 0.6 s^{-1}. Other destruction processes of ozone are therefore needed even in the mesosphere.

THE MESOSPHERIC PHOTOCHEMISTRY

The mesospheric conditions must be considered essentially as an oxygen-hydrogen atmosphere. The principal reactions start from the dissociation of water vapour by various photodissociative channels

$$(J_{OH-H}) \; ; \; H_2O + h\nu(\lambda 240\text{-}175 \text{ nm}) \; \rightarrow \; OH(X^2\Pi) + H(^2S) \tag{26}$$

$$(J_{OH-H}) \; ; \; H_2O + h\nu(Ly\text{-}\alpha) \; \rightarrow \; OH(X^2\Pi) + H(^2S) \; ; \quad 70\% \tag{27}$$

$$(J_{OH-H}) \; ; \qquad\qquad \rightarrow \; OH(A^2\Sigma) + H(^2S) \; ; \quad 8\% \tag{28}$$

$$(J_{H_2-O}) \; ; \qquad\qquad \rightarrow \; H_2(X^1\Sigma_g^+) + O(^1D) \; ; \quad 10\% \tag{29}$$

$$(J_{H-H-O}) \; ; \qquad\qquad \rightarrow \; O(^3P) + 2H(^2S) \; ; \quad 1\% \tag{30}$$
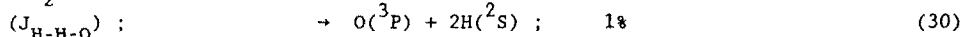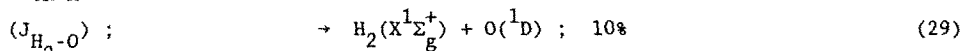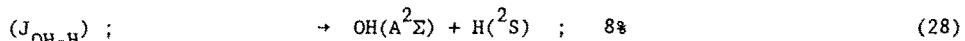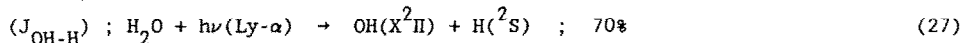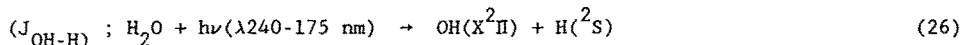
Water vapour photodissociation can be described in the mesosphere by J_{OH-H} and J_{H_2-O}. Nevertheless, the term $a_{H_2O}^* n(O^*)$ taking into account the reaction of the excited oxygen atom with H_2O, must be added for its dissociation in the lower mesosphere.

With the production of H atoms and OH radicals, various reactions become possible. In the mesosphere the principal processes are the production of the perhydroxyl radical

with

$$(a_1) \; ; \; H + O_2 + M \rightarrow HO_2 + M \tag{31}$$

$$a_{1M} = 5.9 \times 10^{-32} \; n(M) \; cm^3 \; s^{-1} \tag{31a}$$

the production of the excited hydroxyl radical

with

$$(a_2) \; ; \; H + O_3 \rightarrow O_2 + OH^* \tag{32}$$

$$a_2 = 1.4 \times 10^{-10} \; e^{-480/T} \; cm^3 \; s^{-1} \tag{32a}$$

leading to the airglow emission in the infrared.

These two reactions are followed by processes involving OH and HO_2

with

$$(a_5) \; ; \; O + OH \rightarrow H + O_2 \tag{33}$$
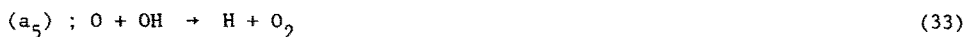
$$a_5 = 2.3 \times 10^{-11} \; e^{40/T} \; cm^3 \; s^{-1} \tag{33a}$$

and

with

$$(a_7) \; ; \; O + HO_2 \rightarrow OH + O_2 \tag{34}$$

$$a_7 = 2.9 \times 10^{-11} \; e^{200/T} \; cm^3 \; s^{-1} \tag{34a}$$

i.e. the first introduction of a catalyst (hydrogen) leading to a loss of atomic oxygen (and ozone).

After its photodissociation, H_2O can be re-formed by the reaction

$$(a_{17}) \; ; \; OH + HO_2 \rightarrow H_2O + O_2 \tag{35}$$

Reactions with O_3 or leading to H_2O_2 can be neglected at mesospheric levels. Reactions between H and HO_2

$$(a_{15}) \; ; \; H + HO_2 \rightarrow OH + OH \tag{36a}$$

$$(a_{20}) \; ; \qquad\qquad \rightarrow H_2O + O \tag{36b}$$

$$(a_{23}) \; ; \qquad\qquad \rightarrow H_2 + O_2 \tag{36c}$$

cannot be important to the general behaviour of the mesosphere. Reactions (36c) must be associated with the photodissociation process (29), both being a mesospheric source of molecular hydrogen.

Above the mesopause, where we must introduce the upper boundary conditions for atomic hydrogen, the transport conditions must be considered. Hence

$$<H> + n(H) \left[a_1 n(M) n(O_2) + a_2 n(O_3) + a_{15} n(HO_2) \right]$$
$$= n(H_2O) \left[J_{OH-H} + 2J_{2H-O} \right] + a_5 n(O) n(OH) + a^*_{H_2} n(O^*) n(H_2) \tag{37}$$

At the mesopause, the lifetime of atomic hydrogen is of the order of 2×10^3 s and increases rapidly in the lower thermosphere but it is only 20 s at 70 km.

It may be added here that the production of H_2 depends strongly on the photodissociation of H_2O. Its mesospheric distribution is given by

$$\langle H_2 \rangle + n(H_2)a^*_{H_2}n(O^*) = n(H)a_{23}n(HO_2) + n(H_2O)J_{H_2-O} \tag{38a}$$

or in its simplest form

$$\langle H_2 \rangle = n(H_2O)J_{H_2-O} \tag{38b}$$

i.e. a continuous production of molecular hydrogen by the photodissociation of water vapour at Lyman-alpha which leads to a transport from its production peak downwards through the lower mesosphere and upwards into the thermosphere.

The rate of change of the concentration of water vapour in the mesosphere can be written :

$$\langle H_2O \rangle + n(H_2O)\left[J_{OH-H} + J_{2H-O} + J_{H_2-O} + a^*_{H_2O}n(O^*)\right] = a_{17}n(OH)n(HO_2) \tag{39}$$

The water vapour dissociation can be described in the mesosphere by the its photodissociation and at the stratopause level by its reaction with the excited atom $O(^1D)$. H_2O is subject to a permanent transport in the mesosphere related to its photodissociation and reformation from the reaction between OH and HO_2. The reaction between H and HO_2 giving $H_2O + O$ was not introduced into (39).

The associated equations for the hydroxyl and hydroperoxyl radicals are

$$\{OH\} + n(OH)\left[a_5n(O) + a_{17}n(HO_2)\right]$$
$$= n(H)a_2n(O_3) + n(HO_2)a_7n(O) + n(H_2)a^*_{H_2}n(O^*) + n(H_2O)\left[J_{OH-H} + 2a^*_{H_2O}n(O^*)\right] \tag{40}$$

and

$$\{HO_2\} + n(HO_2)\left[a_7n(O) + a_{17}n(OH) + a_{15}n(H)\right] = n(H)a_{1M}n(O_2) \tag{41}$$

These equations lead, of course, to

$$\langle H \rangle + 2\langle H_2O \rangle + 2\langle H_2 \rangle + \{OH\} + \{HO_2\} = 0 \tag{42}$$

so that, the rate of change of $n(O)$ in the mesosphere should be written

$$\langle O \rangle + \{O_3\}$$
$$+ 2k_{1M}n^2(O) + n(O_3)\left[2k_3n(O) + a_2n(H)\right]$$
$$+ n(O)\left[a_5n(OH) + a_7n(HO_2)\right]$$
$$+ n(O^*)\left[a^*_{H_2O}n(H_2O) + a^*_{H_2}n(H_2)\right]$$
$$= 2n(O_2)J_2 + n(H_2O)\left[J_{H_2-O} + J_{2H-O}\right] \tag{43}$$

where $k_{1M} = k_1n(M)$ and $k_{2M} = k_2n(M)$.

These equations lead to an expression determining the mesospheric conditions

$$\langle O \rangle + \{O_3\} + \langle H_2O \rangle + \{OH\} + 2k_{1M}n^2(O) + 2k_3n(O)n(O_3) + 2a_5n(O)(OH) = 2n(O_2)J_2 \tag{44a}$$

while

$$\frac{n(O_3)}{n(O)} = \frac{k_{2M}n(O_2)}{J_3 + a_2n(H) + k_3n(O)} \qquad (44b)$$

In applying numerical values in (44) for a standard atmosphere, it can be seen that the ratio $n(O_3)/n(O) = 1$ near 60 km (daytime conditions), i.e. in the lower mesosphere above the stratopause level where photoequilibrium conditions can be assumed for almost all aeronomic parameters. Furthermore, $k_3n(O) < J_3 + a_2n(H)$ and instead of (44b) we see that

$$n(O_3)/n(O) = k_{2M}n(O_2)/[J_3 + a_2n(H)] \qquad (44c)$$

can be introduced into (44) giving the simplest formula for upper mesospheric conditions

$$<O> + <H_2O> + \{OH\} + 2k_{1M}\left[1 + \frac{k_{2M}}{k_{1M}} \cdot \frac{k_3n(O_2)}{J_3 + a_2n(H)}\right]n^2(O) + 2\,a_5n(OH)n(O) = 2n(O_2)J_2 \qquad (44d)$$

This shows the action of the photodissociation of oxygen and of water vapour on the aeronomic behaviour in the mesosphere. Their photodissociation rates must be known with accuracy. For example, the photodissociation frequency of water vapour by Lyman-alpha at the top of the earth's atmosphere is about 5×10^{-6} s^{-1} if the absorption cross-section is of the order of 1.6×10^{-17} cm^2 and the solar irradiance of the order of 3×10^{11} photons cm^{-2} s^{-1}.

Below the mesopause at 75 km (overhead sun) or 80 km (solar zenith angle $= 60°$), the photodissociation lifetime of water vapour due to the action of H Lyman-alpha is less than 200 hours, since $J_{Ly\alpha}(H_2O) > 10^{-6}$ s^{-1} for $N(O_2) = 10^{20}$ cm^{-2}. It is clear that such a short life time must produce a decrease of the H_2O mixing ratio; the reaction between OH and HO_2 cannot by production of H_2O counterbalance its destruction by photodissociation, and the transport conditions cannot always provide an adequate support.

The hydrogen production related to this H_2O photodissociation by Lyman-alpha may be of the order of 10^3 H_2 molecules cm^{-3} sec^{-1} and that due to the reaction H + HO_2 may be of the same order of magnitude.

The photodissociation of H_2O in the region of the Schumann-Runge bands is difficult to determine with precision since the solar flux and the H_2O absorption cross-sections are not known accurately enough. In addition, the transmittance of each O_2 Schumann-Runge band is very sensitive to the temperature. A general uncertainty of about a factor of 2 at the stratopause level is inherent in the various input data. We can say that, for a fixed solar spectral irradiance, it is possible to reach the following uncertainty limits: not better than $\pm$ 10% at $N(O_2) = 10^{19}$ cm^{-2}, $\pm$ 20% at $N(O_2) = 10^{20}$ cm^{-2}, $\pm$ 50% at $N(O_2) = 10^{21}$ and reaching a factor of about 2 at $N(O_2) = 10^{22}cm^{-2}$.

Below the mesopause at 75 km (overhead sun) or 80 km (solar zenith angle $= 60°$), the photodissociation frequency $J_{SRB}(H_2O)$ would be of the order of 2×10^{-7} s^{-1}, i.e. about 10 times less than photodissociation by Lyman-alpha.

In any case, photodissociation at 75 km and above is the leading aeronomic process determining the vertical distribution of water vapour in the upper mesosphere and

lower thermosphere. At the stratopause level, the H_2O photodissociation frequency in the 200-175 nm region is less than 10^{-8} s^{-1}, and the reaction $O(^1D) + H_2O \rightarrow 2$ OH must be taken into account.

As a consequence more atmospheric observations and laboratory experiments with permanent spectral solar irradiances are needed together with general improvement of the accuracy of the various aeronomic parameters.

THE GENERAL PHOTOCHEMICAL EQUATION

In order to write a general equation, we must introduce, simultaneously, all processes involving hydrogen, nitrogen and halogen trace constituents; that is involving H, OH, HO_2, H_2O_2, H_2, H_2O, CH_4 and CO_2, N, NO, NO_2, NO_3, N_2O_5, HNO_3, HNO_4 and N_2O, Cl, ClO, HCl, $ClONO_2$, and HOCl, Br, BrO, HBr, $BrONO_2$ and HOBr,... which can produce or destroy O_3 and O. We use the following symbols for the reaction coefficients : k for O and O_3, J for photodissociation, a for hydrogen, b for nitrogen, c for carbon, d for chlorine, e for bromine (and f for fluorine which will not be introduced here). The corresponding reactions which were considered for their specific role are given in Tables in the Appendix.

Atomic oxygen and ozone concentrations are governed by a general equation such as

$$
\begin{aligned}
&<O_3> + <O> + \{O^*\} \\
&\quad + 2k_{1M}n^2(O) + 2k_3n(O)n(O_3) + n(O_3)\left[a_2n(H) + a_6n(OH) + a_{6c}n(HO_2)\right. \\
&\qquad \left. + b_8n(N) + b_4n(NO) + b_9n(NO_2) + d_2n(Cl) + e_2n(Br)\right] \\
&+ n(O)\left[a_5n(OH) + a_7n(HO_2) + c_9n(H_2CO)\right. \\
&\qquad + b_1n(N) + b_2n(NO) + b_3n(NO_2) + b_{10M}n(NO_2) + b_{15}n(NO_3) \\
&\qquad \left. + d_3n(ClO) + e_3n(BrO) + e_{17}n(Br_2)\right] \\
&+ n(O^*)\left[a^*_{H_2O}n(H_2O) + a^*_{H_2}n(H_2) + c^*_{1a,b}n(CH_4) + b^*_{N_2O}n(N_2O)\right. \\
&\qquad \left. + 2k^*_3n(O_3) + k^*_9n(M) + d^*_{Cl}n(C_xCl_y) + e^*_{Br}n(C_xBr_y)\right] \\
&= 2n(O_2)J_2 + n(H_2O)J_{H_2-O} + n(HO_2)J_{OH-O} + a_{16}n^2(OH) + a_{20}n(H)\,n(HO_2) \\
&\qquad + n(CO_2)J_{CO_2} + n(N_2O)J_{N_2O} + n(NO)J_{NO} + n(NO_2)J_{NO_2} + n(NO_3)J_{NO_2-O} \\
&\qquad + n(N_2O_5)J_{NO_3-NO-O} + n(N)\left[b_{5a}\,n(NO_2) + b_6n(NO) + b_7n(NO_2)\right] \\
&\qquad + n(ClONO_2)\,J_{ClONO-O} + n(BrO)J_{BrO} + n(O_3)J^*_3
\end{aligned}
\tag{45}
$$

In this equation several terms can be neglected; for example, those involving atomic nitrogen which virtually does not exist in the stratosphere under normal conditions. Photoequilibrium conditions can also be immediately adopted for the excited oxygen atom, $O(^1D) = O^*$.

THE HYDROGEN CONSTITUENTS

The principal hydrogen constituent is water vapour whose relative concentration (volume mixing ratio) is between 10^{-6} and 10^{-5} in the stratosphere and mesosphere. Its general equation is written

$$<H_2O> + n(H_2O) \left[J_{OH-H} + J_{H_2O} + a^*_{H_2O} n(O^*) \right]$$

$$= a_{20}n(H)n(HO_2) + n(OH)\left[a_{16}n(OH) + a_{17}n(HO_2) + a_{30}(H_2O_2) \right.$$

$$+ c_2n(CH_4) + c_{17}n(CH_3O_2H) + c_8n(H_2CO) + b_{30}n(HO_2NO_2)$$

$$+ b_{25}n(HNO_2) + b_{27}n(HNO_3) + d_{11}n(HCl) + e_{11}n(HBr) + d_{16a}n(HOCl)$$

$$+ d_{OH}n(C_xH_yCl_z) + \left. e_{OH}n(C_xH_yBr_z) \right] \tag{46}$$

The water vapour photodissociation can be described in the mesosphere by J_{OH-H} and J_{H_2-O} and its dissociation in the stratosphere by the term $a^*_{H_2O}n(O^*)$. Since these three terms are small, there is no chemical equilibrium and H_2O is subject to a permanent transport throughout the stratosphere and mesosphere. If the scatter among the observed profiles indicates a real variability of the H_2O mixing ratio in the atmosphere, it is clear that the transport term must be introduced in the analysis of the water vapour effect in models of stratospheric chemistry, and, in any case, the precise mechanism for any transpsort of H_2O at the various levels of the tropical, mean-latitude and polar tropopause is still unfortunately open to question.

It is known that, above the ozone peak, $a_{17}n(HO_2)n(OH)$ is the principal reformation rate of water vapour. However, the term $c_2n(CH_4)$ and its associate $c_8n(H_2CO)$ must be considered as a permanent production of water vapour in the stratosphere corresponding to dissociative reactions of CH_4. Below the ozone peak, the role of these terms becomes predominant, and the action of HNO_3 and HNO_4 reacting with OH must be added. The other terms are secondary.

Since the maximum average production and re-formation of stratospheric water vapour is of the order of 10^4 cm^{-3} s^{-1}, any transport process of this order of magnitude must be introduced in the determination of the H_2O distribution.

The effect of methane must be introduced in (46). This constituent, with the conventional value of 1.5×10^{-6} for its relative concentration at the tropopause, cannot be re-formed when it is dissociated in the atomosphere. The general equation

$$<CH_4> + n(CH_4)J_{CH_2-H_2} + n(CH_4) \left[c^*_{1a,b}n(O^*) + c_2n(OH) + d_5n(Cl) \right] = 0 \tag{47}$$

shows that there is a permanent upward transport with complete transformation of CH_4 to H_2, H_2O and CO. The CH_4 photodissociation due to Lyman-alpha occurs only in the upper mesosphere, and the destruction processes in the stratosphere are due to its reaction with O^* and OH. The reaction of Cl with CH_4 must be considered since it corresponds to about 10% of the total chemical loss rate of CH_4 which is between 10^3 and 3×10^3 cm^{-3}s^{-1} at almost all stratospheric levels. Several intermediate processes occur before the complete destruction of CH_4 is attained : CH_3, CH_3O_2, H_2CO, HCO, CH_2O_2H formation.

Chemical equilibrium conditions can be introduced for a certain number of constituents since their lifetimes are short enough. Finally, consideration of the formaldehyde molecule, which plays an important role in the trasformation of methane, leads to

$$\{H_2CO\} + n(H_2CO) \left[J_{H-HCO} + J_{H_2-CO} + c_8 n(OH) + c_9 n(O) + d_{10} n(Cl) + e_{10} n(Br) \right]$$

$$= n(CH_4) \left[c^*_{1a,b} n(O^*) + c_2 n(OH) + d_5 n(Cl) \right] \qquad (48)$$

Since J_{H_2CO} is not less than $10^{-5} s^{-1}$ in the stratosphere, photochemical equilibrium conditions in (48) may be introduced in a general analysis.

The carbon monoxide equation is

$$<CO> + n(CO)c_{20}n(OH)$$

$$= n(CO_2)J_{CO_2} + n(CH_4) \left[c^*_{1a,b}n(O^*) + c_2 n(OH) + d_5 n(Cl) + P(CO) \right] \qquad (49)$$

where P(CO) indicates additional productions of carbon monoxide.
The photodissociation of carbon dioxide is a mesospheric process by contrast to the CH_4 oxidation which is a stratospheric process. Since $2 \times 10^{-7} s^{-1} < c_{20}n(OH) < 2 \times 10^{-6} s^{-1}$ in the stratosphere, the transport conditions of carbon monoxide must be introduced, particularly in the lower stratosphere if the transport term $<CO>$ is of the order of 10^3 $cm^{-3} s^{-1}$ corresponding to the order of magnitude of the CH_4 destruction rate.

The remaining molecule, which must be considered in this analysis, is H_2. The general rate of change of its concentration is

$$<H_2> + n(H_2) \left[a_{19}n(OH) + a^*_{H_2}n(O^*) + d_6 n(Cl) \right]$$

$$= n(H_2O)J_{H_2-O} + n(H)a_{23} n(HO_2) + n(CH_4)J_{CH_2-H_2}$$

$$+ c^*_{1b}n(O^*)n(CH_4) + n(H_2CO)J_{H_2-CO} \qquad (50)$$

The H_2 behaviour is completely different in the stratosphere and in the mesosphere. We have seen before that, in the latter region, the production terms correspond to the reaction of H with HO_2, and the photodissociation of H_2O into H_2 and O products. The stratospheric production ensues from the photodissociation of formaldehyde and the reaction of an excited oxygen atom with methane. The stratospheric destruction, represented essentially by the term $a^*_{H_2} n(O^*)$, is very slow and therefore it can be said that H_2 is produced by different processes in the two atmpheric layers. Since its relative concentration at the tropopause level is of the order of 0.5×10^{-6}, it cannot be neglected in a precise stratospheric analysis. In any case, it must be introduced owing to its important role in the mesospheric processes related to atomic hydrogen and hydroxyl radicals.

The H_2 loss term $a_{19}n(OH)$ and $a^*_H n(O^*)$ are the two leading processes with loss rates of the order of 10^3 $cm^{-3} s^{-1}$. Since $c^*_{1b}n(O^*)n(CH_4)$ is small, $\leq 10^2$ $cm^{-3} s^{-1}$, and since the diurnally averaged production rate $n(H_2CO)J_{H_2-CO}$ is not less 10^3 $cm^{-3} s^{-1}$ in the lower stratosphere but decreases with height, the stratospheric production of H_2 is small and its vertical distribution will depend on the transport process $<H_2>$. A precise

observation of H_2 in the lower stratosphere would be a good tracer of the behaviour of the stratospheric products associated with the variation of H_2O and the CH_4 and C_xH_y oxidation.

THE NITROGEN CONSTITUENTS

In the study of nitrogen compounds related to the stratospheric chemistry, several polyatomic molecules such as HNO_3, HNO_2, HNO_4, N_2O_5, NO_3,... must be considered. The most important polyatomic molecule in the stratosphere is nitric acid. It is represented by the equation

$$<HNO_3> + n(HNO_3) \left[J_{HNO_3} + b_{27}n(OH) \right] = b_{22M}n(OH)n(NO_2) + b_{23a}n(HO_2)\,n(NO_3) \qquad (51)$$

Since J_{HNO_3} varies from $10^{-4}\,s^{-1}$ in the neighbourhood of the stratopause to about 5×10^{-7} at lower levels, the long life time of HNO_3 in the solar radiation field in the lower stratosphere leads to the possibility of atmospheric transport while in the middle and upper stratosphere photochemical equilibrium conditions prevail. The lower boundary conditions in the stratosphere must be important in determining the behaviour of HNO_3, and hence its action in the ozone chemistry. Because of the major uncertainties associated with the tropopause variation with latitude and with the general rainout problem of all acids in the upper troposphere, its stratospheric removal with distribution in time and space is not yet accurately known.

The equation for nitrous acid, HNO_2, corresponds to photochemical equilibrium conditions since its photodissociation is sufficiently rapid. Hence,

$$\{HNO_2\} + n(HNO_2) \left[J_{OH-NO} + b_{25}n(OH) \right] = b_{21M}n(OH)n(NO) \qquad (52)$$

As far as HO_2NO_2 is concerned, we may write

$$<HNO_4> + n(HO_2NO_2) \left[J_{OH-NO_3} + J_{HO_2-NO_2} + b_{28Mc}n(M) + b_{30}n(OH) \right] = b_{28M}n(HO_2)n(NO_2) \qquad (53)$$

indicating that its stratospheric behaviour should be almost parallel to that of HNO_3. However, the products of the photolysis of HNO_4 are not yet known.

The NO_3 molecule, which has a very short lifetime of not more than 100 s is always in photochemical equilibrium. Its equation can be written

$$\{NO_3\} + \{N_2O_5\} +$$
$$n(NO_3) \left[J_{NO_2-O} + J_{NO-O_2} + b_{11}n(NO) + b_{15}n(O) + b_{23a}n(HO_2) + b_{23b}n(OH) \right]$$
$$= n(NO_2) \left[b_9n(O_3) + b_{10M}n(O) \right] + b_{27}n(OH)n(HNO_3)$$
$$+ n(HO_2NO_2)J_{OH-NO_3} + n(ClONO_2)J_{Cl-NO_3} + n(BrONO_2)J_{Br-NO_3} \qquad (54)$$

In (54), the terms corresponding to the photochemical equation of N_2O_5 have not been included. This molecule has the equation :

$$\{N_2O_5\} + n(N_2O_5) \left[J_{N_2O_5} + b_{12c}n(M) \right] = b_{12M}n(NO_2)n(NO_3) \qquad (55)$$

Since $J_{N_2O_5}$ cannot be greater than $5 \times 10^{-5}\,s^{-1}$, the photoequilibrium equation may be used for general conditions, but not for an analysis of a diurnal variation.

Finally, the ozone chemistry in the stratosphere will depend on the behaviour of both NO and NO_2 which are related as shown by the aeronomic equations

$$\langle NO \rangle + n(NO) \left[J_{NO} + b_{2M}n(O) + b_4 n(O_3) + b_6 n(N) + b_{11}n(NO_3) \right.$$

$$\left. + b_{21M}n(OH) + b_{29}n(HO_2) + c_5 n(CH_3O_2) + d_{4a}n(ClO) + e_{4a}n(BrO) \right]$$

$$= n(NO_2) \left[J_{NO_2} + b_3 n(O) \right] + n(NO_3)J_{NO-O_2} + P_a(NO)$$

$$+ n(HNO_2)J_{OH-NO} + P(NO) + 2b_{NO}^* n(O^*)n(N_2O) + n(N_2O_5)J_{NO_3-NO-O}$$

$$+ n(N) \left[b_{1M}n(O) + b_{5b}n(OH) + b_7 n(O_2) + b_8 n(O_3) \right] \qquad (56)$$

and

$$\{NO_2\} + n(NO_2) \left[J_{NO_2} + b_3 n(O) + b_{5a}n(N) + b_9 n(O_3) + b_{10M}n(O) + b_{12M}n(NO_3) \right.$$

$$\left. + b_{22M}n(OH) + b_{28M}n(HO_2) + d_{13M}n(ClO) + e_{13M}n(BrO) \right]$$

$$= n(NO) \left[b_{2M}n(O) + b_4 n(O_3) + 2b_{11}n(NO_3) + b_{29}n(HO_2) + c_5 n(CH_3O_2) \right.$$

$$\left. + d_{4a}n(ClO) + e_{4a}n(BrO) \right] + b_{25}n(OH)n(HNO_2)$$

$$+ n(NO_3) \left[J_{NO_2-O} + b_{23b}n(OH) + b_{15}n(O) \right] + n(HNO_3)J_{OH-NO_2}$$

$$+ (HNO_4) \left[J_{HO_2-NO_2} + b_{28Mc}n(M) + b_{30}n(OH) \right] + n(N_2O_5) \left[J_{NO_2-NO_3} + b_{12Mc}n(M) \right] \qquad (57)$$

To complete this analysis of the principal aeronomic reactions of the nitrogen oxides chemistry, the equation of atomic nitrogen must be also written; it is, with $\{N\} = 0$,

$$n(N) \left[b_{1M}n(O) + b_{5a}n(NO_2) + b_{5b}n(OH) + b_6 n(NO) + b_7 n(O_2) + b_8 n(O_3) \right] = n(NO)J_{NO} + P_a(N) \qquad (58)$$

In (58) the entities $P_a(NO)$ and $P_a(N)$ may represent natural or artificial production processes corresponding to a perturbation.

It is clear that the action of atomic nitrogen is negligible at low stratospheric levels, and that several reactions included in (56) and (57) cannot be significant. The principal stratospheric loss rate for NO given by $n(NO)b_4 n(O_3)$, is greater than 10^6 $cm^{-3}s^{-1}$ in the major part of the stratosphere. However, an interaction with hydrogen and halogen compounds is introduced by the terms $b_{29}n(HO_2)$ and $d_4 n(ClO)$, respectively. Their NO loss rate may reach more than 10% of that due to O_3. The other loss terms in (56) represent less than 1% of the total loss of NO.

The NO_2 loss is due to its photodissociation and also, in the upper stratosphere, to its reaction with atomic oxygen. The total loss rate of nitrogen dioxide is greater than 10^6 $cm^{-3}s^{-1}$ in the major part of the stratosphere and the various rates which are involved in determining the ratio $n(NO_2)/n(NO)$ must be assessed in relation to this high value. Consequently, all $\{XY\}$ terms corresponding to a diurnal variation may be neglected since the times which are involved are of the order of a few hundred seconds. When the transports of HNO_3 and HNO_4 do not reach 10^4 $cm^{-3}s^{-1}$, $\langle HNO_3 \rangle$ and $\langle HNO_4 \rangle$ can be neglected above a certain stratospheric altitude.

The conventional ratio

$$n(NO_2)/n(NO) = b_4 n(O_3)/J_{NO_2} \qquad (59)$$

which was first used several years ago as an aeronomic parameter must now be written in the form

$$n(NO) \left[b_4 n(O_3) + b_{29} n(HO_2) + c_5 n(CH_3O_2) + d_{4a} n(ClO) + e_{4a} n(BrO) \right]$$

$$= n(NO_2) \left[J_{NO_2} + b_3 n(O) \right] \qquad (60)$$

in order to indicate clearly the possible action of hydrogen and halogen compounds on the numerical value of the ratio $n(NO_2)/n(NO)$.

THE HALOGENATED CONSTITUENTS

Chlorine, bromine and fluorine in the stratosphere behave differently because the reactions of the halogen atoms, Cl, Br and F with CH_4 and H_2 and of HCl, HBr and HF with OH, are different : Cl reacts slowly with CH_4; F reacts rapidly, and Br does not react; HF does not react with OH although HCl and HBr do react.

The chlorine atoms are rapidly in chemical equilibrium and

$$\{Cl\} = n(Cl) \quad \left[d_2 n(O_3) + d_5 n(CH_4) + d_6 n(H_2) + d_7 n(HO_2) + d_8 n(H_2O_2) + d_{9b} n(NO_3) \right.$$

$$\left. + d_{10a} n(H_2CO) + \ldots d_{10e} n(C_2H_6) + d_{10f} n(C_3H_8) \right]$$

$$= n(HCl) d_{11} n(OH) + n(ClONO_2) J_{Cl-NO_3} + n(HOCl) J_{OH-Cl}$$

$$+ n(Cl_x - Cl_y) \left[J_{C_x-Cl_y} + d_1^* n(O^*) \right] + 2n(Cl_2) \, J_{Cl_2}$$

$$+ n(Cl_2O) J_{Cl_2O} + n(Cl_2O_2) J_{Cl-ClOO} + n(NOCl) J_{NO-Cl} + n(ClONO) J_{Cl-NO_2}$$

$$+ n(ClO) \left[d_3 n(O) + d_{4a} n(NO) + d_{4b_1} n(OH) + e_5 n(BrO) \right] \qquad (61)$$

in which $C_x Cl_y$ represent all possible halocarbons leading to chlorine atoms by photodissociation. This equation is the basic atmospheric equation which must be used to determine the concentration of chlorine atoms establishing the ClO and HCl concentrations. The chlorine monoxide can be also considered practically in chemical equilibrium and,

$$\{ClO\} + n(ClO) \left[d_3 n(O) + d_{4a} n(NO) + d_{4b_{1,2}} n(OH) + d_{13M} n(NO_2) + d_{15} n(HO_2) + e_5 n(BrO) \right]$$

$$= n(Cl) \left[d_2 n(O_3) + d_{7b} n(HO_2) + d_{9b} n(NO_3) \right] + n(ClONO_2) J_{ClO-NO-O} \qquad (62)$$

In (62) certain photodissociations of $ClONO_2$ or HOCl which could lead to ClO are not considered and their reactions with OH, O and Cl have not be included since they cannot be important.

In the stratosphere, the hydrochloric acid is not in chemical equilibrium at all altitudes, and the general equation must be written

$<HCl> + n(HCl) \ d_{11}n(OH)$

$$= n(Cl) \left[d_5n(CH_4) + d_6n(H_2) + d_{7a}n(HO_2) + d_8n(H_2O_2) + d_{10a}n(H_2CO) + \ldots\right.$$

$$\left. + d_{10e}n(C_2H_6) + d_{10f}n(C_3H_8)\right] + n(ClO) \ d_{4b_2}n(OH) \tag{63}$$

The photodissociation of HCl is very slow, less than 10^{-7} s^{-1} in the stratosphere. Its reaction with OH leads to a lifetime which may be more than 10^6 s in the lower stratosphere and reaches about 10^5 s near the stratopause. There is therefore a problem of stratosphere-troposphere exchange with its substantial uncertainties through the rainout of HCl below the tropopause. $ClONO_2$ and HOCl must be introduced in the stratospheric chlorine chemistry, and their equations have the forms :

$\{ClONO_2\} +$

$$n(ClONO_2) \left[J_{ClNO_3} + d_{14a_{1,2,3}}n(OH) + d_{14b_{1,2,3}}n(O) + d_{14c}n(Cl)\right]$$

$$= d_{13M}n(ClO) \ n(NO) \tag{64}$$

$\{HOCl\} +$

$$n(HOCl) \left[J_{OH-Cl} + d_{16a}n(OH) + d_{16c}n(Cl)\right] = d_{15}n(ClO) \ n(HO_2) \tag{65}$$

In (64), J_{ClONO_2} corresponds to two photodissociation processes. The principal photodissociation process of chlorine nitrate is

$$ClONO_2 + h\nu \rightarrow Cl + NO_3 \tag{66a}$$

with a quantum yield of the order of 0.9 at wavelengths less than 260 nm where the absorption cross-section is of the order of 3×10^{-19} cm^2. At 300 nm and 350 nm were the absorption cross-sections are of the order of 2×10^{-20} cm^2 and 2×10^{-21} cm^2, respectively, the photochemical transition

$$ClONO_2 + h\nu \rightarrow ClONO + O \tag{66b}$$

is observed with a quantum yield of the order of 0.1. Chlorine nitrate must play a permanent role in stratospheric chemistry and therefore can be a temporary reservoir of chlorine. Photolytic action is the principal destruction process of $ClONO_2$ so it is possible to reduce photochemical equations (64) and (65) of $ClONO_2$ and HOCl to

and
$$\{ClONO_2\} + n(ClNO_3)J_{ClNO_3} = d_{13M}n(ClO) \ n(NO) \tag{64a}$$

$$\{HOCl\} + n(HOCl)J_{HOCl} = d_{15}n(ClO) \ n(HO_2) \tag{65a}$$

In (65), HOCl is photodissociated as indicated to OH and Cl by radiation of wavelengths greater than 300 nm since the absorption cross-sections at 310 and 365 nm are of the order of 6×10^{-20} and 6×10^{-21} cm^2, respectively.

Various species such as $Cl_2O_2,\ldots$ which may play a role, for example, in the polar stratosphere are not considered here since they are described in other articles. In fact, Cl_2O_2 with absorption cross-sections of the order of 10^{-18} and 10^{-19} cm^2 at 300 and 340 nm, respectively, is subject to photodissociation after 10^2- 10^3 s. ClONO, NOCl, ClO_3, OClO, ClOO, Cl_2O and Cl_2, for example, are also photodissociated aftter 10^2-10^3 s

and are not considered as primary chlorine constituents under normal stratospheric conditions. The photodissociaton of many other constituents starting from $CCl_4, \ldots CHCl_3, \ldots CF_3Cl_3, \ldots$ must be determined with accuracy in the laboratory to establish the exact vertical production of Cl and F atoms with latitude and seasons. The action of the excited oxygen atom $O(^1D)$ on the chlorofluorocarbons with a reaction coefficient generally between 1 and 3×10^{-10} cm^3 s^{-1} may be considered at low levels where the photodissociation is inappreciable. Finally, all reactions of chlorine compounds involving hydrogen atoms and OH radicals must be considered when their activition energies are not too high.

If we compare the atmospheric bromine chemistry with that of chlorine, we note differences shown by the atomic bromine and bromine monoxide equations :

$\{Br\} +$

$$n(Br) \left[e_2 n(O_3) + e_7 n(HO_2) + e_{10} n(H_2CO)\right]$$

$$= n(BrO) \left[J_{BrO} + e_3 n(O) + e_{4a} n(NO) + e_{4b_1} n(OH) + e_5 n(ClO) + 2e_6 n(BrO)\right]$$

$$+ e_{11} n(OH)\, n(HBr) + n(BrONO_2) J_{Br-NO_3} + n(HOBr) J_{OH-Br}$$

$$+ n(Br_2) \left[J_{Br_2} + e_{17} n(O) + e_{18} n(OH)\right] + n(C_x \cdot\cdot Br_y) \left[J_{C_x \cdots Br_y} + e_1 n(OH) + e_1^* n(O^*)\right] \tag{67}$$

The bromine monoxide equation takes the form

$\{BrO\} +$

$$n(BrO) \left[J_{BrO} + e_3 n(O) + e_{4a} n(NO) + e_{4b_{1,2}} n(OH) + e_5 n(ClO)\right.$$

$$\left. + 2e_6 n(BrO) + e_{13M} n(NO_2) + e_{15} n(HO_2)\right]$$

$$= e_2 n(Br) n(O_3) + e_{17} n(O) n(Br_2) \tag{68}$$

Since the absorption cross-sections of BrO are of the order of 2×10^{-18} and 5×10^{-19} cm^2 at 300 nm and 375 nm, respectively, a lifetime of the order of 100 s in the solar radiation field indicates that photodissociation of bromine monoxide is an important aeronomic process. Br_2 must be considered only as transitory constituent since its photodissociation frequency is of the order of 10^{-2} s^{-1}.

The hydrobromic acid is not in chemical equilibrium at all stratospheric altitudes and, therefore,

$$<HBr> + n(HBr) \left[J_{HBr} + e_{11} e(OH) = n(Br) \left[e_7 n(HO_2) + e_{10} n(H_2CO)\right]\right.$$

$$+ n(BrO) e_{4b_2} n(OH) \tag{69}$$

The photodissociation process of HBr is very slow corresponding to a lifetime of the order of 2×10^5 to 10^6 s in the middle stratosphere. In the lower stratosphere it is not photodissociated and the reaction with OH is the chemical loss process. But for the formation of HBr a precise comparaison of the action of Br and BrO is needed. Rainout with stratosphere-troposphere exchange at the tropopause level must be taken into account. In addition to the preceding equations, $BrONO_2$ and HOBr must also considered :

$$\{BrONO_2\} + n(BrONO_2)J_{BrNO_3} - e_{13M}n(NO_2)n(BrO) \tag{70a}$$

and

$$\{HOBr\} + n(HOBr)J_{HOBr} - e_{15}n(HO_2)n(BrO) + e_{18}n(OH)n(Br_2) \tag{70b}$$

in which J_{BrNO_3} and J_{HOBr} may represent different photodissociation products. Reactions of $BrONO_2$ and HOBr with other constituents have been neglected, but could be introduced without modifying our analysis. Since the lifetime of $BrONO_2$ and HOBr in the stratospheric solar radiation field is of the order of 1000 s, no transport effect is considered.

THE FLUORINE PROBLEM

The fluorine compounds have not been included in the general discussion of aeronomic reactions related to the ozone photochemistry since F and FO concentrations are very small. However, the stratospheric abundance of HF which seems to increase when the number density of HCl seems to be almost constant is a problem which has not been discussed with all possible consequences such as the rainout action below the tropopause. Since the reactions of fluorine atoms with H_2O, CH_4 and H_2 are fast (not less than 10^{-11} $cm^3 s^{-1}$), the atomic fluorine concentrations must be very small. Perhaps, a reaction such as $F + O_2 + M \rightarrow M + FO_2$ is important which could give a ratio $n(F)/n(FO)$ less than 10^{-9} near the tropopause. Thus, the final process of hydrofluoric acid

$$\langle HF\rangle + n(HF) \; f_{1a}^{*}n(O^{*}) =$$
$$n(F) \left[f_5 n(CH_4) + f_6 n(H_2) + f_7 n(H_2O)\right] \tag{71}$$

will act only above a certain altitude in the stratosphere where n(F) is increasing. Even if there is no reaction between OH and HF, fast reaction between OH and HBr and important reaction between OH and HCl, the OH concentration does not seem to be the only aeronomic parameter to be considered. The removal mechanisms at the tropopause by reaction or rainout require more systematic studies.

EFFECT OF HALOGEN OXIDES

Confining attention to the terms corresponding to chlorine and bromine in the general equation (45), we may write for stratospheric conditions

$$\langle O_3\rangle + \{O\} + \{O^*\} + \{ClO\} + \{BrO\} + \ldots +$$
$$2n(O)\left[d_3 n(ClO) + e_3 n(BrO)\right] +$$
$$n(O^*)\left[d_{Cl}^{*}n(C_xCl_y) + e_{Br}^{*}n(C_xBr_y)\right] +$$
$$n(ClO)\left[d_{4a}n(NO) + d_{4b_{1,2}}n(OH) + d_{13m}n(NO_2) + d_{15}n(HO_2) + 2e_5 n(BrO)\right] +$$
$$n(BrO)\left[e_{4a}n(NO) + e_{4b_{1,2}}n(OH) + e_{13M}(NO_2) + e_{15}n(HO_2) + 2e_6 n(BrO)\right]$$
$$= \ldots + 2n(ClONO_2)(J_{ClO-NO-O}) + n(Cl)\left[d_{7b}n(HO_2) + d_{9b}n(NO_3)\right] \tag{72}$$

when the aeronomic equations (62) for ClO are adopted without any simplification.

On the other hand, if we consider the effect of water vapour by considering H_2O (equation 46) with OH

{OH} +

$$n(OH) \left[a_5 n(O) + a_6 n(O_3) + 2a_{16} n(OH) + 2a_{16M} n(OH) + a_{17} n(HO_2) \right.$$

$$+ a_{30} n(H_2O_2) + c_{20} n(CO) + c_2 n(CH_4) + c_8 n(H_2CO) + c_{17} n(CH_3O_2H)$$

$$+ b_{5b} n(N) + b_{21M} n(NO) + b_{22M} n(NO_2) + b_{23b} n(NO_3) + b_{25} n(HNO_2) + b_{27} n(HNO_3) + c_{30} n(HO_2NO_2)$$

$$+ d_{OH} n(C_x H_y Cl_z) + e_{OH} (C_x H_y Br_z)$$

$$\left. + d_{4b} n(ClO) + d_{11} n(HCl) + e_{4b} n(BrO) + e_{11} n(HBr) \right]$$

$$= n(H) \left[a_2 n(O_3) + 2a_{15} n(HO_2) \right] + n(HO_2) \left[a_{6c} n(O_3) + a_7 n(O) + J_{HO_2} + b_{29} n(NO) + d_{7b} n(Cl) \right]$$

$$+ n(H_2) n^*_{H_2} n(O^*) + n(H_2O) \left[J_{OH-H} + 2a^*_{H_2O} n(O^*) \right]$$

$$+ 2n(H_2O_2) J_{H_2O_2} + n(CH_4) c^*_{1a} n(O^*) + c_9 n(H_2CO) n(O)$$

$$+ n(HNO_2) J_{HNO_2} + n(HNO_3) + n(HO_2NO_2) J_{OH-NO_3}$$

$$+ n(HOCl) J_{OH-Cl} + d_{12} n(O) n(HCl) + n(HOBr) J_{OH-Br} \tag{73}$$

The principal loss terms of OH leading to H and HO_2, represented by $a_5 n(O)$ and $a_6 n(O_3)$, are of the order of 10^{-1} s^{-1} in the stratosphere, and {OH} = 0 in (73) in a general analysis.

A numerical analysis of the various terms of equation (73) shows that the ratio $n(HO_2)/n(OH)$ is maintained in chemical equilibrium, since the OH and HO_2 reaction rates with O and O_3 lead to values from about 10^5 cm^{-3} s^{-1} in the lower stratosphere to more than 10^6 cm^{-3} s^{-1} in the upper stratosphere. Hence, in the expression (73) for the determination of $n(OH)/n(HO_2)$, chemical equilibrium conditions can be applied except when <H_2O>, <CH_4>, <H_2> or <HNO_3> reach values greater than 10^4 cm^{-3} s^{-1}. Furthermore, their numerical values are small compared with the principal rate values affecting OH and HO_2.

The principal terms of (73) may be written, for a preliminary determination of stratospheric conitions, without the action of halogen compounds :

$$a_2 n(H) n(O_2) + n(HO_2) \left[a_{6c} n(O_3) + a_7 n(O) + b_{29} n(NO_2) \right]$$

$$= n(OH) \left[a_5 n(O) + a_6 n(O_3) + c_{20} n(CO) \right] \tag{73a}$$

The term involving atomic hydrogen may be neglected in a preliminary calculation and this simplified form must be adopted as the initial equation; nevertheless, $a_2 n(H) n(O_3)$ must be included at and above 40 km.

At the stratopause level, we may write as a first approximation

$$a_2 n(H) n(O_3) + n(HO_2) a_7 n(O) = n(OH) a_5 n(O) \tag{73b}$$

and at the tropopause level, when the transport terms are not considered, i.e., <XY> less than 10^4 cm^{-3} s^{-1}

$$n(HO_2) \left[a_{6c} n(O_3) + b_{29} n(NO_2) \right] = n(OH) \left[a_6 nO_3) + c_{20} n(CO) \right] \tag{73c}$$

Although the ratio $n(HO_2)/n(OH)$ can be easily calculated, except in the lower stratosphere where transport processes are significant near the tropopause, the determination of the absolute value of the OH (or HO_2) concentration is difficult, particularly below the ozone peak, because of the interaction of various constituents. A numerical analysis of the various terms of the general equation (73) indicates that the total stratospheric loss rate is of the order of 10^4 cm^{-3} s^{-1}, and also that there is a strong influence of HNO_3 and HCl below the ozone peak. Since the transport processes can affect HNO_3 and HCl in the lower stratospshere, the absolute concentrations of the OH and HO_2 radicals may change if $<HNO_3>$ or $<HCl>$ are not too far from a value of the order of 10^4 cm^{-3} s^{-1}.

Finally, we may write

$$<H_2O> + (OH) + n(H_2O) \left[J_{H_2-O} + J_{O-2H} \right]$$

$$+ n(OH) \left[a_5 n(O) + a_6 n(O_3) + a_{16} n(OH) + 2a_{16M} n(OH) + c_{20} n(CO) \right]$$

$$+ n(OH) \left[b_{5b} n(N) + b_{21M} n(NO) + b_{22M} n(NO_2) + b_{23b} n(NO_3) \right]$$

$$+ n(OH) \left[d_{4b} n(ClO) + e_{4b} n(BrO) + e_{18} n(Br_2) \right]$$

$$= a_2 n(O_3) n(H)$$

$$+ n(HO_2) \left[a_{6c} n(O_3) + a_7 n(O) + J_{HO_2} + 2a_{15} n(H) + a_{20} n(H) + b_{29} n(NO_2) + d_7 n(Cl) \right]$$

$$+ c_{1a}^* n(O^*) n(CH_4) + c_9 n(H_2CO) n(O) + n(O^*) \left[a_{H_2O}^* n(H_2O) + a_{H_2}^* n(H_2) \right]$$

$$+ n(HNO_2) J_{HNO_2} + n(HNO_3) J_{OH-NO_2} + n(HNO_4) J_{OH-NO_3} +$$

$$+ n(HOCl) J_{OH-Cl} + n(HOBr) J_{OH-Br} \tag{74}$$

The simultaneous action of the hydrogen and halogen constituents on O_3 and O can be represented :

$$<O_3> + <O> + (O^*) + <H_2O> + (OH) + (ClO) + (BrO) + \ldots$$

$$2n(O_3) a_6 n(OH)$$

$$+ 2n(O) \left[a_5 n(OH) + d_3 n(ClO) + e_3 n(BrO) \right]$$

$$+ n(O^*) \left[c_{1b} n(CH_4) + d_{Cl}^* n(C_x Cl_y) + c_{Br}^* n(C_x Br_y) + k_{9M}^* n(M) \right]$$

$$+ n(OH) \left[2a_{16M} n(OH) + c_{20} n(CO) + b_{5b} n(N) + b_{21M} n(NO) + b_{22M} n(NO_2) \right.$$

$$\left. + b_{23b} n(NO_3) + 2d_{4b} n(ClO) + 2e_{4b} n(BrO) + e_{18} n(Br_2) \right]$$

$$+ n(ClO) \left[d_{4a} n(NO) + d_{13M} n(NO_2) + d_{15} n(HO_2) + 2e_5 n(BrO) \right]$$

$$+ n(BrO) \left[e_{4a} n(NO) + e_{13M} n(NO_2) + d_{15} n(HO_2) + 2e_6 n(BrO) \right]$$

$$= \ldots + n(HO_2) \left[2J_{HO_2} + 2a_{15} n(H) + 2a_{20} n(H) + b_{29} n(HO_2) + d_{7b} n(Cl) \right]$$

$$+ n(HNO_2) J_{HNO_2} + n(NHO_3) J_{OH-NO_2} + n(HNO_4) J_{OH-NO_3} + n(HOCl) J_{OH-Cl} + n(HOBr) J_{OH-Br}$$

$$+ 2n(ClONO_2) J_{ClO-NO-O} + n(Cl) \left[d_7 n(HO_2) + d_{9b} n(NO_3) \right] \tag{75}$$

Before concluding this analysis of the interaction of the various constituents, the effect of the nitrogen compounds on O_3 and O may be represented :

$$<O_3> + <O> + \{O^*\} + \{N\} + \{NO_2\} + 2\{N_2O_5\} + \{NO_3\} + <NO_3> + <HNO_4>$$

$$+\ldots+ n(NO_2)\left[d_{13M}n(ClO) + e_{13M}n(BrO)\right]$$

$$+ n(O_3)\left[2b_8n(N) + b_9n(NO_2)\right]$$

$$+ n(O)\left[2b_{1M}n(N) + 2b_3n(NO_2) + b_{10M}n(NO_2) + b_{15}n(NO_3)\right]$$

$$+ n(N)\left[b_{4a}n(NO_2) + b_{5b}n(OH)\right]$$

$$= n(NO)\left[2J_{NO} + b_{11}n(NO_3) + b_{29}n(HO_2) + c_5n(CH_3O_2)\right]$$

$$+ n(NO)\left[d_{4a}n(ClO) + e_{4a}n(BrO)\right]$$

$$+ n(ClONO_2)J_{Cl-NO_3} + n(BrONO_2)J_{Br-NO_3} \qquad (76)$$

A comparison of the various rates shows that the most important terms in the stratosphere are $(>10^5 \text{ cm}^{-3}\text{ s}^{-1})$ $n(NO_2)J_{NO_2}$, $b_4n(O_3)n(NO)$, $b_3n(O)n(NO_2)$, $a_6n(O_3)(OH)$, $a_5n(O)n(OH)$, $a_7n(O)n(HO_2)$, $d_4n(ClO)n(O)$, $d_3n(ClO)n(O)$, $d_3n(Cl)n(O_3)$ and $b_{29}n(NO)n(HO_2)$. For rates less than $10^4\text{cm}^{-3}\text{ s}^{-1}$ and particularly less than $10^3\text{ cm}^{-3}\text{s}^{-1}$, all terms must be introduced in the analysis.

STRATOSPHERIC OZONE EQUATION

Taking all preceding equations related to the various chemical constituents in the stratosphere into account, the general equation (45) adapted to aeronomic conditions can be approximated by

$$<O_3> + <HO_2> + \{OH\} + 2<HNO_3> + <HNO_4> + \{NO_2\} + 2\{NO_3\} + 2\{N_2O_5\} + \{HNO_2\}$$

$$+ \{ClO\} + 2\{ClONO_2\} + \{HOCl\} + \{BrO\} + 2\{BrONO_2\} + \{BrOCl\}$$

$$+ 2\left[k_3n(O) + a_6n(OH)\right]n(O_3)$$

$$+ 2\left[a_5n(OH) + b_3n(NO_2) + d_3n(ClO) + e_3n(BrO)\right]n(O)$$

$$+ 2\left[d_{4b}n(OH) + e_5n(BrO)\right]n(ClO) + 2\left[e_{4b}n(OH) + e_6n(BrO)\right]n(BrO)$$

$$= 2n(O_2J_2) + <CO>$$

$$+ 2\left[n(H_2O_2)J_{H_2O_2} + 2n(HO_2)\left[J_{HO_2} + \{a_{15} + a_{20}\}n(H) - 2a_{16M}n^2(OH)\right]\right.$$

$$+ 2n(NO)\left[J_{NO} + b_{29}n(HO_2) + c_5n(CH_3O_2)\right] + \ldots \qquad (77)$$

This equation shows the processes of destruction of ozone: directly by two reactions of O_3 with O and OH, by four reactions of O with OH, NO, ClO and BrO and, indirectly, by perturbations resulting from reactions of ClO and BrO with OH anf BrO. As far as the actions of the ClO (or BrO) reactions with OH and BrO are concerned, they should be compared with the reactions of OH with O and of ClO with O, respectively, in order to determine the importance of their perturbation. In a particular diurnally averaged model, $n(ClO)d_{4b}n(OH)$ is about 1% of the rate of OH with O_3 and, therefore, is of only minor importance.

The ozone behaviour may depend on the transport of several constituents. However, the effects of HOBr, $BrONO_2$, HOCl, $ClONO_2$, ..., N_2O_5 can be neglected since photochemical conditions can be used in a general analysis. The permanent transport of water vapour must be less than 10^5 to 10^4 H_2O molecules cm^{-3} s^{-1} in the lower stratosphere and less than 10^6 cm^{-3} s^{-1} (less than 10%) in the middle stratosphere if it is to be neglected. As far as CO and HNO_3 are concerned, their possible effect cannot be neglected without due consideration, but the transport conditions apply certainly in the lower stratosphere.

The additional production terms must be compared with the normal production term $2n(O_2)J_2$ which decreases rapidly below 25 km. Terms which may reach values between 10^6 and 10^5 cm^{-3} s^{-1} below 20 km are important since $n(O_2)J_2$ reaches, for an overhead sun, about 10^5 cm^3 s^{-1} at 15 km, about 10^6 cm^3 s^{-1} at 20 km and about 10^7 at 25 km. For a solar zenith angle χ corresponding to sec $\chi - 2$, the corresponding values of $n(O_2)J_2$ are only about 10^4 near 20 km and 10^6 between 25 and 30 km. In a specific diurnally averaged model, the absolute value of 5×10^5 cm^{-3} s^{-1} decreases to 5×10^4 and 5×10^3 cm^{-3} s^{-1} at 20 and 17.5 km, respectively. If we consider the bracketed groups of the second member of (77), we may conclude that few terms are appreciable. In the first group, terms involving OH and HO_2 can be neglected and only $2n(H_2O_2)J_{H_2O_2}$ need to be kept so as to show that such a term is a production term of the order of 10^3 cm^{-3} s^{-1}. In the second bracketed group, J_{NO} is negligible as compared with $b_{29}n(HO_2)$, which is significant as a production term since $2b_{29}n(HO_2)n(NO)$ can be greater than 10^5 cm^{-3} s^{-1}. The term $c_5n(CH_3O_2)n(NO)$ must be also considered. In fact, these two terms are fundamental terms in the tropospheric chemistry where NO_x and C_xH_y are important minor constituents.

SUMMARY AND CONCLUSIONS

The general equation (45), with all the essential production and loss processes of ozone and atomic oxygen, involves a number of reactions of hydrogen, nitrogen and halogen constituents which have strong interactions. It is easily shown that the ratios $n(HO_2)/n(OH)$, $n(NO_2)/n(NO)$, $n(ClO)/n(Cl)$ and $n(BrO)/n(Br)$ rapidly reach chemical equilibrium in a sunlit atmosphere, since the principal processes leading to their formation require reaction times less than 100 s. in the stratospshere. Furthermore, all transport processes with rates less than 10^4 cm^{-3} s^{-1} in the middle stratosphere, and less than 10^3 cm^{-3} s^{-1} in the lower stratosphere, do not play any role in determining the values of the above ratios. Substituting their equilibrium values in (45) leads to different general equations in the stratosphere, and in the mesosphere. By virtue of these substitutions, it is easy to obtain a simplified form of the general equation which is, in the stratosphere,

$$<O_3> + <H_2O> + 2<HNO_3> + <HNO_4>$$

$$+ 2n(O_3)\left[k_3n(O) + a_6n(OH)\right]$$

$$+ 2n(O)\left[a_5n(OH) + b_3n(NO_2) + d_3n(ClO) + e_3n(BrO)\right]$$

$$+ 2n(ClO)\left[d_{4b}n(OH) + e_5n(BrO)\right] + 2n(BrO)\left[e_{4b}n(OH) + e_6n(BrO)\right]$$

$$= 2n(O_2)J_2 + 2n(NO)b_{29}n(HO_2) + 2n(H_2O_2)J_{H_2O_2} + <CO> \qquad (78a)$$

or, if OH is replaced by HO_2,

$<O_3> + <HNO_3>$

$$+ 2n(O_3) \left[k_3 n(O) + a_2 n(H) + a_{6c} n(HO_2) \right]$$

$$+ 2n(O) \left[a_7 n(HO_2) + b_3 n(NO_2) + d_3 n(ClO) + e_3 n(BrO) \right]$$

$$+ 2n(ClO) \left[d_{15a} n(HO_2) + e_5 n(BrO) \right]$$

$$+ 2n(BrO) \left[e_{15a} n(HO_2) + e_6 n(BrO) \right] + 2n(H_2O_2) J_{H_2O_2}$$

$$= 2n(O_2) J_2) + 2n(OH) \left[b_{27} n(HNO_3) + c_{20} n(CO) \right] + 2n(NO) c_5 n(CH_3O_2)$$

$$+ <H_2O> + <CO> + 2<CH_4> \tag{78b}$$

With equation (78) we hence have convenient general expressions for the rate of change of stratospheric ozone concentration in which the actions of hydrogen, nitrogen and halogen compounds are represented respectively by OH (or HO_2), NO_2, and ClO and BrO. However, equilibrium conditions have been imposed, in these equations, for the following constituents :

$$\{OH\} = \{HO_2\} = \{H_2O_2\} =)NO_2\} = \{NO_3\} = \{N_2O_5\} = \{HNO_2\} = \{ClO\} = \{ClONO_2\}$$

$$= \{HOCl\} = \{BrO\} = \{BrONO_2\} =)BrOH\} = 0 \tag{79}$$

In a stratospheric model, such steady state solutions correspond to diurnally averaged conditions.

In the stratosphere $n(O_3) > n(O)$, but in the mesosphere atomic oxygen plays the leading role in which an important action of hydrogen compounds is involved. Equation (45) becomes, in its simplest form,

$<O> + <H_2O>$

$$+ 2 \left[k_{1M} + \frac{k_3 k_{2M}}{J_{3M}} \right] n^2(O) + 2a_5 n(OH) n(O) = 2n(O_2) J_2 \tag{80}$$

The OH concentration is related to its production by H_2O, CH_4 and H_2 by an expression in which the values of the HO_2 and H concentrations must be introduced. The effect of atomic hydrogen begins in the upper stratosphere and is important in the whole mesosphere. On the other hand, the ratio $n(HO_2)/n(OH)$ varies from a very simple form, $n(HO_2)/n(OH) = 1$, near the stratopause to more complicated and different forms in the mesosphere and stratosphere. In the lower stratosphere below the ozone peak, the absolute value of the OH (and also HO_2) depends on several parameters in which HNO_3, HCl, and HNO_4 are involved in addition to the reactions of OH and HO_2. If we try to use numerical values, it is clear that the reaction coefficients of OH with HO_2, H_2O_2, HNO_3, HNO_4 and HCl must be known accurately.

Since the OH loss rates below the ozone peak are not greater than 10^3 cm^{-3} s^{-1}, the transport processes affecting HNO_3, ... must be very slow if they are to be neglected in the determination of the OH concentration. Finally, it should be noticed that the value of both the OH concentration and its variation depend strongly on the behaviour of H_2O dissociation in the stratosphere. Very little is known about the absolute OH concentration below the ozone peak.

The nitrogen dioxide concentration cannot be determined without a knowledge of the nitric oxide concentration. The various equations indicate that, not only the exact photodissociation rate of NO_2, but also the production of NO must be known in order to obtain an absolute value for the NO_2 concentration. From the various groups of equations, we obtain

$$<NO> + <HNO_3> + <HNO_4> + \{N\} + \{NO_2\} + \{NO_3\} + \{N_2O_5\} + \{ClONO_2\} + \{BrONO_2\}$$

$$+ 2n(N) \left[b_5 n(NO_2) + b_6 n(NO) \right]$$

$$= 2n(N_2O) b_{NO}^* n(O^*) + P(NO) + P(N) \tag{81}$$

In the lower stratosphere $<NO> = \{NO\} = 0$, since the NO loss time is of the order of 100 s., and (81) becomes

$$<HNO_3> + <HNO_4> = 2n(N_2O) b_{NO}^* n(O^*) + P(NO) \tag{82}$$

$n(N)$ being so small that its reaction rates are negligible. However, in the mesosphere, equation (81) leads to, $\{HNO_3\} = 0$, and

$$<NO> + 2b_6 n(N)n(NO) = P(NO) + P(N) \tag{83}$$

the NO production from the oxidation of N_2O being negligible. Substituting the simplest value of the atomic nitrogen concentration in (83), the rate of change of NO becomes

$$<NO> + \frac{2b_6 J_{NO}}{b_7 n(O_2)} \ n^2(NO) = P(NO) + P(N) \tag{84}$$

This equation indicates that the behaviour of nitric oxide in the mesosphere differs from that in the stratosphere where the normal production is due to the oxidation of N_2O by the excited oxygen atom $O(^1D)$ and where it is necessary to determine the vertical distribution of N_2O, i.e. to solve the equation

$$<N_2O> + n(N_2O) \left[J_{N_2-O} + b_{N_2O}^* n(O^*) \right] = b_{5a} n(N)n(NO_2) = 0 \tag{85}$$

As far as the halogen monoxides ClO and BrO are concerned, the use of the ratios $n(ClO)/n(Cl)$ and $n(BrO)/n(Br)$ requires a knowledge of all the production processes of atomic chlorine and bromine, i.e. the exact distribution of the sources of these two atoms (photodissociation processes and subsequent products) in the stratosphere. In such an analysis, after neglecting three minor terms Cl is directly related to HCl through

$$n(Cl) \left[d_5 n(CH_4) + d_6 n(H_2) + d_7 n(HO_2) + d_8 n(H_2O_2) + d_{10} n(H_2CO) \right]$$

$$+ \{Cl\} + \{ClO\} + \{ClONO_2\} + \{HOCl\}$$

$$= n(HCl) \left[J_{HCl} + d_{11} n(OH) + d_{12} n(O) \right] + \Sigma n(C_x Cl_y) J_{C_x Cl_y} \tag{86}$$

where $<Cl> = \{Cl\}$ since the terms between brackets lead to a value which falls from 10^{-1} s^{-1} to 10^{-3} s^{-1} between the tropopause and the stratopause. Substituting the value of HCl in (86), in order to complete the solution of the problem, gives

$$<HCl> + \{Cl\} + \{ClO\} + \{ClONO_2\} + \{HOCl\} = \Sigma n(C_xCl_y)J_{C_xCl_y} \qquad (87)$$
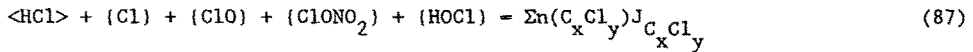
which indicates that the HCl transport process must correspond to the dissociation rate of the injected chlorofluorocarbons. Here again, the behaviour of HCl in the lower stratosphere is closely related to the value of the OH concentration. It is well to recall once more that very little is known about the absolute values of several chemical parameters particularly in the lower stratosphere below the ozone peak. In reality, there is always an uncertainty and this causes a difficulty which affects not only the treatment of each group of equations corresponding to hydrogen, nitrogen or halogen compounds, but also the general treatment that is needed to complete the solutions of the important practical problems of stratospheric chemistry.

BIBLIOGRAPHY

References can be found in :
FABRY, Ch. (1929) Rapport de la réunion de l'ozone et de l'absorption atmosphérique, Gerlands Beitr. Geophys., 24, 1-77.
1. FABRY, Ch., Introduction.
2. DOBSON, G.M.B., Atmospheric Ozone.
3. HOELPER, O., Diskussion mit Dr. Dobson.
4. LINKE, F., Bermerkung über die Mitteilung des Herrn Dobson.
5. BUISSON, H. Comparaison des mesures d'ozone faite à Marseille et à Arosa.
6. RUEDY, R., Observations sur l'ozone faites au Canada.
7. CHALONGE, D. et GÖTZ, P., Comparaison entre les teneurs en ozone de la haute atmosphère pendant le jour et pendant la nuit.
8. HOELPER, O., Über die spektrale Durchlässigkeit der Atmosphäre.
9. BUISSON, H., Spectrographe double pour la mesure de l'ozone atmosphérique.
10. GÖTZ, ., Der Aroser Ultraviolettsspektrograph;
11. DEMBER, H., Ein lichtelektrisches Universalspektrometer.
12. GÖTZ, P. Ozonbestimmung ohne intensitäatsmessung;
13. FABRY, Ch., Remarques sur les coefficients d'absorption de l'ozone.
14. LADENBURG, R., Bemerkung über die Absorptionskoeffizienten des Ozons.
15. LAMBREY, L. et CHALONGE, D., Structure de la bande d'absorption ultra-violette de l'ozone.
16. RUEDY, R., Note on the study of atmospheric ozone.
17. ROSSELAND, S., A theoretical remark on the distribution of ozone in the atmosphere.
18. LINDHOLM, F., Note sur l'absorption de l'ozone dans la partie infrarouge du spectre solaire.
19. GOWAN, E.H., The effect of ozone on the temperature of the upper atmosphere.
20. LINKE, F., Bermerkung über die Mitteilung von Gowan.
21. ROSSELAND, S., On the temperature of the upper atmosphere.
22. ANGSTRÖM, A., La quantité d'ozone dans l'atmosphère et sa relation avec les problèmes climatologiques.
23. BJERKNES, V., Sur les relations entre l'ozone et les mouvements de la troposphère.
24. CHAPMAN, S., On the variations of ozone in the upper atmosphere.
25. DAWSON, L.H., GRANATH, L.P. and HULBURT, E.O., The attenuation of ultraviolet light by the lower atmosphere.
26. REGENER, E., Ozon und Leithähigkeit der Atmosphäre.
27. WHIPPLE, F.J.W., Researchers on the transmission of air waves to great distances.
28. GUTENBERG, B. Bemerkung über die Temperatur der Stratosphäre.
29. Conclusions.

GÖTZ, F.W.P., (1938) Die verticale Verteilung des atmosphärischen Ozons, Ergebnisse der kosmischen Physik, $\underline{3}$, 253-325, with 318 references.

DOBSON, G.M.B. (1963) Exploring the Atmosphere, Clarendon Press, Oxford. Chapter 6 Ozone in the Atmosphere, pp. 103-127.

NICOLET, M. (1979). Etude des réactions chimiques de l'ozone dans la stratosphère, Institut Royal Météorologique de Belgique, 53p. with 750 references, and

NICOLET, (M) (1975) Stratospheric Ozone : An Introduction to its Study, Rev. Geophys. Space Phys., $\underline{13}$, 593-636.

The last publication is :

ATKINSON, R., BAUCH, D.L., COX, R.A., HAMPSON, Jr., R.F., KERR, J.A., and TROE, J., Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, J. Phys. Chem. Ref. Data, $\underline{18}$, 881-1097,

with data sheets for 360 thermal and photochemical reactions.

APPENDIX. MAIN REACTIONS

Reactions Coefficient ($cm^3 s^{-1}$)	Reaction
J_2 ; 3 spectral ranges	$O_2 + h\nu(\lambda < 242 \text{ nm}) \rightarrow O + O$
$k_1 = 4.7 \times 10^{-33}(300/T)^2 \, n(M)$	$O + O + M \rightarrow O_2 + M$
$k_2 = 6 \times 10^{-34}(300/T)^{2.3} \, n(M)$	$O + O_2 + M \rightarrow O_3 + M$
$k_3 = 8.0 \times 10^{-12} \exp[-2060/T]$	$O + O_3 \rightarrow 2O_2$
J_3 ; 3 spectral ranges	$O_3 + h\nu \rightarrow O_2 + O$
J_3^* ; Hartley band	$O_3 + h\nu(\lambda < 310 \text{ nm}) \rightarrow O_2(^1\Delta_g) + O(^1D)$
$k_M^* = 4.3 \times 10^{-11}$	$O(^1D) + N_2 \text{ and } O_2 \rightarrow O(^3P) + M$
$a_{H_2O}^* = 1.7 \times 10^{-10}$	$O(^1D) + H_2O \rightarrow 2OH$
$a_{CH_4}^* = (1.4 \pm 0.2) \times 10^{-10}$	$O(^1D) + CH_4 \rightarrow CH_3 + OH$
$= 1.5 \times 10^{-11}$	$\rightarrow H_2 + H_2CO$
$a_{H_2}^* = (1.0 \pm 0.1) \times 10^{-10}$	$O(^1D) + H_2 \rightarrow H + OH$
$J_{H_2O}, \ J_{CH_4}, \ J_{H_2O_2}$	
$a_1 = 2.1 \times 10^{-32} \exp[290/T] \, n(M)$	$H + O_2 + M \rightarrow HO_2 + M$
$= 5.9 \times 10^{-32} \, n(M)$	
$a_2 = 1.4 \times 10^{-10} \exp[-480/T]$	$H + O_3 \rightarrow O_2 + OH^*$
$a_5 = 2.3 \times 10^{-11} \exp[40/T]$	$O + OH \rightarrow O_2 + H$
$a_7 = 2.9 \times 10^{-11} \exp[200/T]$	$O + HO_2 \rightarrow O_2 + O$
$a_6 = 1.9 \times 10^{-12} \exp[-1000/T]$	$O_3 + OH \rightarrow O_2 + HO_2$
$a_{6c} = 1.4 \times 10^{-14} \exp[-600/T]$	$O_3 + HO_2 \rightarrow 2O_2 + OH$
$a_{17} = 4.8 \times 10^{-11} \exp[250/T]$	$OH + HO_2 \rightarrow H_2O + O_2$
$a_{27} = 2.2 \times 10^{-13} \exp[600/T]$	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
$a_{30} = 2.9 \times 10^{-12} \exp[-160/T]$	$OH + H_2O_2 \rightarrow H_2O + HO_2$
$c_2 = 3.7 \times 10^{-12} \exp[-1820/T]$	$OH + CH_4 \rightarrow H_2O + CH_3$
$c_{20} = 1.5 \times 10^{-13}$	$CO + OH \rightarrow CO_2 + H$
$a_{15} = 7.2 \times 10^{-11}$	$H + HO_2 \rightarrow OH + OH$
$a_{20} = 2.4 \times 10^{-12}$	$\rightarrow H_2O + O$
$a_{23} = 5.6 \times 10^{-12}$	$\rightarrow O_2 + H_2$

APPENDIX (followed)

J_{H_2-CO}	$H_2CO + h\nu \rightarrow CO + H_2$
J_{H-HCO}	$H_2CO + h\nu \rightarrow HCO + H$
$c_8 = 1.6 \times 10^{-11} \exp[-110/T]$	$OH + H_2CO \rightarrow HCO + H_2O$
$c_9 = 3.1 \times 10^{-11} \exp[-1500/T]$	$O + H_2CO \rightarrow HCO + OH$
$c_5 = 4.2 \times 10^{-12} \exp[180/T]$	
$c_7 = 3.0 \times 10^{-13} \exp[720/T]$	$NO + CH_3O_2 \rightarrow CH_3O + NO_2$
$c_{17} = 1 \times 10^{-11}$	$HO_2 + CH_3O_2 \rightarrow CH_3O_2H + O_2$
$b^*_{N_2O}$; $(1.2 \pm 0.2) \times 10^{-10}$	$OH + CH_3O_2H \rightarrow CH_3O_2 + H_2O$
$\quad\quad (0.5 \pm 0.1) \times 10^{-10}$	
$\quad\quad (0.7 \pm 0.1) \times 10^{-10}$	$O(^1D) + N_2O \rightarrow N_2 + O_2$
$b_3 = 6.5 \times 10^{-12} \exp[120/T]$	$\quad\quad\quad\quad \rightarrow NO + NO$
$b_4 = 1.8 \times 10^{-12} \exp[-1370/T]$	$O + NO_2 \rightarrow NO + O_2$
$b_{29} = 3.7 \times 10^{-12} \exp[240/T]$	$O_3 + NO \rightarrow NO_2 + O_2$
$J_{NO_2} \geq 5 \times 10^{-3} \, s^{-1}$	$HO_2 + NO \rightarrow OH + NO_2$
$b_{22} = 2.6 \times 10^{-30} (300/T)^3 \, n(M)$	$NO_2 + h\nu \, (\lambda > 300 \, nm) \rightarrow NO + O$
$b_{27} = 3.4 \times 10^{-15} \exp[778/T]$	$OH + NO_2 + M \rightarrow HNO_3 + M$
$J_{HNO_3} \, (10^{-4}$ to $5 \times 10^{-7} \, s^{-1})$	$OH + HNO_3 \rightarrow H_2O + NO_3$
$b_9 = 1.2 \times 10^{-13} \exp[-2450/T]$	$HNO_3 + h\nu (\lambda < 320 \, nm) \rightarrow OH + NO_2$
$J_{NO_3} \geq 10^{-1} \, s^{-1}$	$O_3 + NO_2 \rightarrow NO_3 + O_2$
	$NO_3 + h\nu \rightarrow NO_2 + O$
	$\quad\quad\quad\quad NO + O_2$
$b_{12} = 2.7 \times 10^{-30} (300/T)^{3.4} \, n(M)$	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$
$J_{N_2O_5}$ (when $\lambda > 300 \, nm$)	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$
$b_{28} = 1.8 \times 10^{-31} \, n(M) \, (300/T)^{3/2}$	$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$
$J_{HO_2NO_2}$	$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2$?
	$\quad\quad\quad\quad OH + NO_3$
$d_{1a} = J_{XCl_x}$ (photodissociation))	$XCl_x + h\nu \rightarrow XCl_{x-1} + Cl$
$d^*_{1a} = 10^{-11} \, cm^3 \, s^{-1}$	$XCl_x + O^* \rightarrow XCl_{x-1} + ClO$
$d_{1b} = ...$	$XCl_xH_y + OH \rightarrow XCl_xH_{y-1} + H_2O$
$d_2 = 2.7 \times 10^{-11} \exp[-257/T]$	$Cl + O_3 \rightarrow O_2 + ClO$
$d_3 = 3.8 \times 10^{-11}$	$ClO + O \rightarrow O_2 + Cl$
$d_{4a} = 6.2 \times 10^{-12} \exp[294/T]$	$ClO + NO \rightarrow NO_2 + Cl$
$d_{4b} = 1 \times 10^{-11} \exp[120/T]$	$ClO + OH \rightarrow O_2 + HO_2$
$\quad\quad < 0.1 \, d_{4b}$	$ClO + OH \rightarrow O_2 + HCl$
$d_5 = 9.6 \times 10^{-12} \exp[-1350/T]$	$Cl + CH_4 \rightarrow CH_3 + HCl$
$d_6 = 3.7 \times 10^{-11} \exp[-1300/T]$	$Cl + H_2 \rightarrow H + HCl$
$d_{7a} = 1.8 \times 10^{-11} \exp[170/T]$	$Cl + HO_2 \rightarrow O_2 + HCl$
$d_{7b} = 4.1 \times 10^{-11} \exp[-450/T]$	$\quad\quad\quad\quad \rightarrow OH + ClO$
$d_8 = 1.1 \times 10^{-11} \exp[-980/T]$	$Cl + H_2O_2 \rightarrow HO_2 + HCl$
$d = 2 \times 10^{-11}$	$Cl + NO \rightarrow NO + ClO$

$d_{10a} = 8.2 \times 10^{-11} \exp[34/T]$

$d_{11} = 2.4 \times 10^{-12} \exp[-330/T]$

$d_{13} = 6.7 \times 10^{-31} n(M) (300/T)$

J_{ClONO_2}

$d_{15} = 4.6 \times 10^{-13} \exp[710/T]$

J_{HOCl}

$e_{1a} = J_{XBr_x}$ (photodissociation)

$e_{1a}^* = 10^{-11} cm^3 s^{-1}$

$e_{1b}^* = \ldots$

$e_2 = 1.7 \times 10^{-11} \exp[-800/T]$

$e_3 = 3.0 \times 10^{-11}$

$e_{4a} = 8.7 \times 10^{-12} \exp[260/T]$

$e_{4b} = 10^{-11}$

$e_5 = 1.6 \times 10^{-12} \exp[426/T]$

      $5.8 \times 10^{-12} \exp[168/T]$

$e_6 = 1.1 \times 10^{-12} \exp[168/T]$

$e_7 = 1.4 \times 10^{-11} \exp[-590/T]$

$e_{10} = 1.7 \times 10^{-11} \exp[-800/T]$

$e_{11} = 1.1 \times 10^{-11}$

J_{BrONO_2} ($\sim 10^{-3}$s)

$e_{13} = 5 \times 10^{-31} (300/T)^3 n(M)$

$e_{15} = 5 \times 10^{-12}$

$f_2 = 2.8 \times 10^{-11} \exp[-225/T]$

$f_3 = 5 \times 10^{-11}$

$f_4 = 2.6 \times 10^{-11}$

$f_5 = 3 \times 10^{-10} \exp[-400/T]$

$f_6 = 1.2 \times 10^{-10} \exp[-470/T]$

$f_7 = 0.6 \times 10^{-11} \exp[-28/T]$

$f_8 = 4.3 \times 10^{-33} n(M) \times (300/T)^{1.4}$

$f_9 = 5 \times 10^{-11}$

$f_{10} = 1 \times 10^{-10}$

$f_{11} = 0$

$f_{13} = 8 \times 10^{-31} n(M) \times (300/T)^{3/4}$

$\ldots\ldots\ldots\ldots$

$f_{16a} = 4 \times 10^{-12} \exp[-400/T]$

$f_{16b} = 3 \times 10^{-12} \exp[-500/T]$

$f_{16c} = 3.5 \times 10^{-12} \exp[-400/T]$

$Cl + H_2CO \rightarrow HCO + HCl$

$HCl + OH \rightarrow H_2O + Cl$

$ClO + NO_2 + M \rightarrow ClONO_2 + M$

$ClONO_2 + h\nu$ ($\lambda < 400$ nm) $\rightarrow Cl + NO_3$

                      $\rightarrow Cl + O + NO$

$ClO + HO_2 \rightarrow HOCl + O_2$

$HOCl + h\nu \rightarrow OH + Cl$

$XBr_x + h\nu \rightarrow XBr_{x-1} + Br$

$XBr_x + O^* \rightarrow XBr_{x-1} + BrO$

$XBr_xH_y + OH \rightarrow XBr_xH_{y-1} + H_2O$

$Br + O_3 \rightarrow O_2 + BrO$

$BrO + O \rightarrow O_2 + Br$
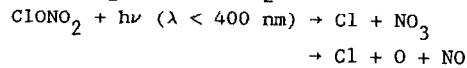
$BrO + NO \rightarrow NO_2 + Br$

$BrO + OH \rightarrow HO_2 + Br$

           $\rightarrow HBr + O_2$

$BrO + ClO \rightarrow Br + OClO$

            $\rightarrow Br + Cl + O_2$

$BrO + BrO \rightarrow 2 Br + O_2$

            $\rightarrow Br_2 + O_2$

$Br + HO_2 \rightarrow O_2 + HBr$

$Br + H_2CO \rightarrow HCO + HBr$

$OH + HBr \rightarrow H_2O + Br$

$BrONO_2 + h\nu \rightarrow Br + NO_2$

$NO_2 + BrO + M \rightarrow BrONO_2 + M$

$HO_2 + BrO \rightarrow HOBr + O_2$

$F + O_3 \rightarrow FO + O_2$

$FO + O \rightarrow O_2 + F$

$FO + NO \rightarrow NO_2 + F$

$F + CH_4 \rightarrow CH_3 + HF$

$F + H_2 \rightarrow H + HF$

$F + H_2O \rightarrow OH + HF$

$F + O_2 + M \rightarrow FO_2 + M$

$FO_2 + O \rightarrow FO + O_2$

$O(^1D) + HF \rightarrow OH + F$

$OH + HF \rightarrow F + H_2O$

$FO + NO_2 + M \rightarrow FNO_3 + M$

$\ldots\ldots\ldots\ldots$

$NO + CF_3O_2 \rightarrow CF_3O + NO_2$

$NO + CF_2ClO_2 \rightarrow CF_2ClO + NO_2$

$NO + CFCl_2O_2 \rightarrow CFCl_2O + NO_2$