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**Modeling of stratospheric ions : a first attempt**

by

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## FOREWORD

This paper has been presented at the 9th Annual meeting of the European Geophysical Society held in Leeds (Great-Britain), August 1982. It will appear in the Annales Geophysicae.

## AVANT-PROPOS

Cet article résume une communication présentée à la 9e réunion annuelle de la Société Européenne de Géophysique qui s'est tenue à Leeds (Grande Bretagne) en août 1982. Il sera publié dans Annales Geophysicae.

## VOORWOORD

Dit artikel is een samenvatting van een mededeling die gedaan werd op de 9e Algemene Vergadering van de "European Geophysical Society" die plaats vond in Leeds (Groot-Brittanië) in augustus 1982. Het zal gepubliceerd worden in Annales Geophysicae.

## VORWORT

Dieser Aufsatz stellt die Zusammenfassung einer Mitteilung während der 9. Allgemeinen Tagung der Europäischen Geophysicalischen Gesellschaft in Leeds (Gross-Britannien) im August 1982 da. Er wird veröffentlicht in den Annales Geophysicae.

# MODELING OF STRATOSPHERIC IONS : A FIRST ATTEMPT

by

G. BRASSEUR(\*) and A. CHATEL(\*\*)

## Abstract

Several observations of positive and negative ions around 35 km have shown the complexity of the ion chemistry in the stratosphere. The presence of cluster ions such as  $H^+X_n(H_2O)_m$  (with probably  $X = CH_3CN$ ) has been detected. Negative ions such as  $NO_3^-$ ,  $(HNO_3)_n^-$  and  $HSO_4^-$ ,  $(H_2SO_4)_n^-$ ,  $(HNO_3)_m^-$  are also present. The chemical kinetics of these ions is still poorly known. The purpose of the paper is to present and discuss preliminary results obtained with a model which simulates the behavior of stratospheric ions.

## Résumé

Des observations effectuées aux environs de 35 km d'altitude ont montré la complexité de la chimie des ions dans la stratosphère. La présence d'agrégats du type  $H^+X_n(H_2O)_m$  (où X est probablement  $CH_3CN$ ) a été détectée. Des ions négatifs du type  $NO_3^-$ ,  $(HNO_3)_n^-$  et  $HSO_4^-$ ,  $(H_2SO_4)_n^-$ ,  $(HNO_3)_m^-$  sont également présents. La cinétique chimique des ions n'est pas encore bien connue. Un modèle décrivant le comportement des ions stratosphériques a cependant été établi, sur base de certaines hypothèses. Les résultats préliminaires sont discutés dans cet article.

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## Samenvatting

Waarnemingen verricht op hoogtes rond 35 km hebben de complexiteit van de ionen-chemie in de stratosfeer aangetoond. Clusters van het type  $H^+X_n(H_2O)_m$  (met X waarschijnlijk gelijk aan  $CH_3CN$ ) werden gedetecteerd. Negative ionen van het type  $NO_3^-(HNO_3)_n$  en  $HSO_4^-(H_2SO_4)_n$  werden eveneens gevonden. De kinetische chemie van de ionen is nog onvoldoende gekend. Op basis van bepaalde hypothesen werd nochtans een model ontwikkeld dat het gedrag van de stratosferische ionen weergeeft. In dit artikel worden de preliminaire resultaten besproken.

## Zusammenfassung

Beobachtungen auf einer Höhe von ungefähr 35 km zeigten eine sehr grosse Komplexität der stratosphärischen Ionen-Chemie. Aggregate des Types  $H^+X_n(H_2O)_m$  wurden identifiziert wobei X sehr wahrscheinlich  $CH_3CN$  ähnlich ist. Negative Ionen des Types  $NO_3^-(HNO_3)_n$  und  $HSO_4^-(H_2SO_4)_n$  sind ebenfalls identifiziert. Obwohl die kinetische Theorie der Ionen-Chemie noch nicht genügend gekannt ist, ist ebenwohl, dank bestimmten Hypothesen, ein Modell entwickelt worden, das das Benehmen der stratosphärischen Ionen tatsächlich beschreibt. In dieser Aufsatz werden die vorhergehenden Ergebnisse besprochen.

## 1. INTRODUCTION

The identification of ions in the stratosphere has become technically possible only in the recent years after the development of balloon borne mass spectrometers. The available measurements of positive ion composition have to be attributed to Arnold et al (1977; 1978; 1982) and Arijs et al (1978; 1980; 1982). The observations made in the altitude range of 33-37 km reveal the presence of two distinct families of ion species with more or less the same abundance : (1) the proton hydrates (PH) which are clusters in the form of  $H_3O^+(H_2O)_n$  and (2) the non-proton hydrates (NPH) whose chemical structure can be written as  $H^+X_l(H_2O)_n$ , X being a molecule with a proton affinity exceeding that of water vapor. Arijs et al (1980) have derived unambiguously from their high resolution spectra that the mass of the X molecule should be equal to 41 amu and that the most likely candidate for this molecule is acetonitrile ( $CH_3CN$ ) as suggested by Arnold et al (1978). The proton affinity of  $CH_3CN$  is 187.4 kcal whereas that of water vapor is 168.9 kcal only. The atmospheric budget of acetonitrile as well as its stratospheric concentration is not yet known.  $CH_3CN$  is frequently used as an industrial solvent and it could also be produced by combustion processes.

The chemical composition of negative ions has also been derived from mass spectrometric observations (Arnold and Henschen, 1978; Arijs et al, 1981; 1982; Mc Crumb and Arnold, 1981; Arnold et al, 1981; 1982; Viggiano and Arnold, 1981). These in situ measurements indicate that the major ions are probably clusters belonging to two different families, namely  $HSO_4^-(H_2SO_4)_l(HNO_3)_m$  and  $NO_3^-(HNO_3)_n$ . This underlines the important role played by sulfuric acid and nitric acid in the formation of stratospheric negative ions and the expected relation with the aerosol layers.

Up to now, due to the limited knowledge of the chemical processes involving stratospheric ions, no detailed model of the ionic composition below 50 km has been established. Only partial calculations have been presented to explain some observations. The purpose of this paper is to attempt to produce a global model of the ions in the stratosphere. Because of the large amount of uncertainties in the chemical data, such a model remains preliminary. Many assumptions have still to be made and for example the values of some rate constants have been "tuned" until the calculated and observed ion concentration were in good agreement. The interest of such a model however is to show that, with reasonable assumptions, the adopted chemical scheme can explain the available observations. An other objective is to analyze the relative importance of the different reaction paths and to determine which parameters have the largest influence on the concentration values.

## 2. THE ION SCHEME

The ionization in the stratosphere is due to the action of galactic cosmic rays. The corresponding rate of ion-pair formation can be calculated from the expression suggested by Heaps (1978). When applied to a geomagnetic latitude of 46°, corresponding to the site of Aire sur l'Adour where most observations are made, the Heaps formula becomes

$$Q = 7.1 \times 10^{-18} \text{ [M]} \quad (1)$$

above the altitude of 30 km and

$$Q = 1.7 \times 10^{-20} [M]^{1.15} \quad (2)$$

between 18 and 30 km. In these expressions, [M] is the total concentration expressed in  $\text{cm}^{-3}$  and Q the ionization rate given in  $\text{cm}^{-3} \text{s}^{-1}$ .

The main loss process of the ions is the recombination between positive and negative charges. The corresponding recombination coefficient  $\alpha$  can be deduced either from observational data (Gringel *et al*, 1978; Rosen and Hofman, 1981) or from laboratory work (Smith and Church, 1977; Smith and Adams, 1982). Its value can also be established from theoretical considerations (Bates, 1982). In the present model, we have adopted the expression

$$\alpha(\text{cm}^3 \text{s}^{-1}) = 6 \times 10^{-8} (300/T)^{0.5} + 2 \times 10^{-26} [M] (300/T)^4 \quad (3)$$

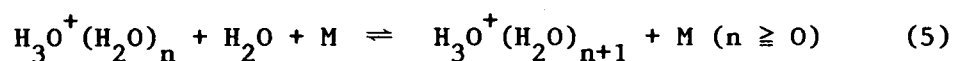
which provides values lying between those suggested by Bates (1982) and Smith and Adams (1982). In this formula, T is the temperature expressed in K. Introducing the electro-neutrality condition, one can immediately derive that the total concentration of positive and negative ions is given by

$$n^+ = n^- = (Q/\alpha)^{1/2} \quad (4)$$

and is equal to  $6000 \text{ cm}^{-3}$  at 20 km,  $4400 \text{ cm}^{-3}$  at 30 km,  $2800 \text{ cm}^{-3}$  at 40 km and  $1500 \text{ cm}^{-3}$  at 50 km, if the temperature profile of the US Standard atmosphere (1966) is used.

## 2.1. Positive ions

Since the primary ion  $N_2^+$  exchanges its electrical charge instantaneously with  $O_2$ , one can consider that each ionization leads to the formation of an ionized oxygen molecule. The subsequent chemistry has been described in several papers and in particular by Ferguson (1979) and Arnold (1980).  $O_2^+$  reacts with  $O_2$  to form  $O_4^+$  which can be hydrated to produce  $O_2^+ \cdot H_2O$  and subsequently  $H_3O^+$ . The other hydrates with higher orders are obtained by supplementary hydrations



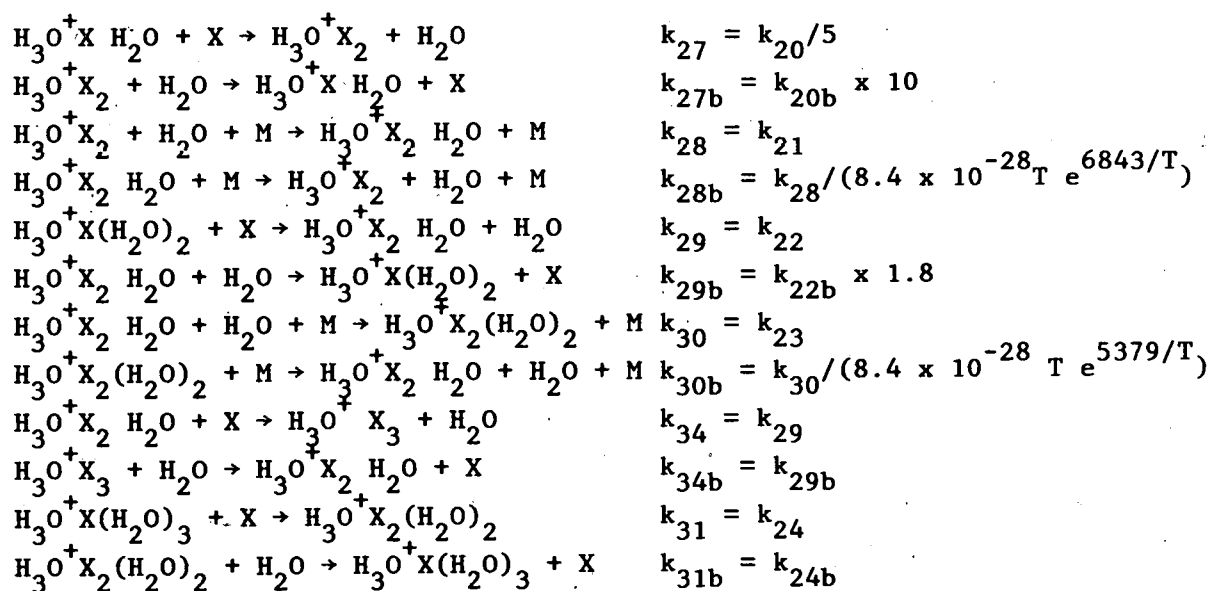
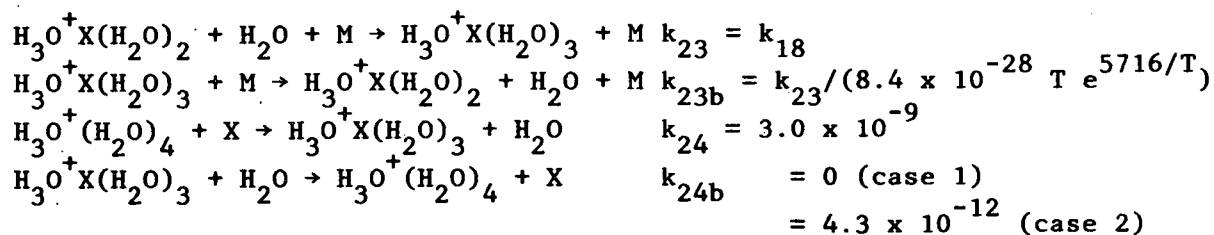
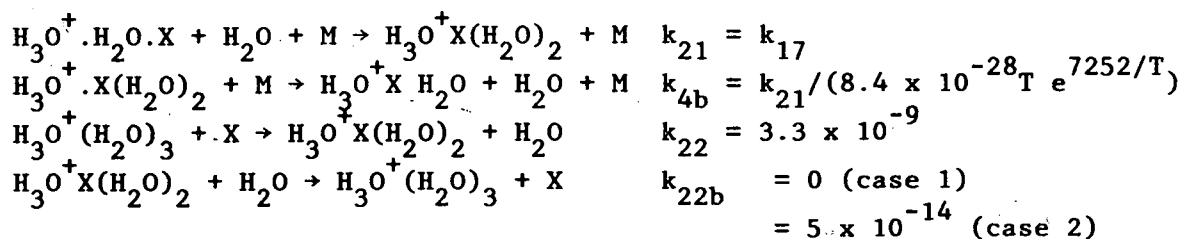
which are characterized by a forward reaction rate  $k_f$  and a reversed rate constant  $k_r$  associated to the thermal dissociation. The ratio  $[H_3O^+(H_2O)_{n+1}]/[H_3O^+(H_2O)_n]$  is proportional to the equilibrium constant  $K_{n+1,n} = k_f/k_r$  which varies intensively with the temperature. The values of these parameters reactions  $k_{12}$  to  $k_{18}$  in table 1 are taken from the recent paper by Lau et al (1982).

The non-proton hydrates  $H_3O^+ X_\ell(H_2O)_n$  are formed by reactions of PH with an X molecule and subsequent conversions between X and  $H_2O$ . Different candidates have been suggested for X (e.g. Na OH by Ferguson, 1978) but since the mass of this molecule is unambiguously equal to 41 a.m.u., according to Arijs et al (1980), the most likely candidate for X seems to be acetonitrile ( $CH_3CN$ ). Other non-proton hydrates, namely  $H_3O^+ Y_\ell(H_2O)_n$ , appear in the spectra obtained by Henschen and Arnold (1981) and Arnold and Henschen (1982), where Y is a molecule with mass  $32 \pm 1$ . This molecule has been tentatively identified as methanol ( $CH_3OH$ ) by Henschen and Arnold (1981). The proton affinity of  $CH_3OH$  ( $182 \text{ kcal mole}^{-1}$ ) is larger than that of water vapor but smaller than that of acetonitrile. Therefore  $H_3O^+ Y(H_2O)_n$  should react with  $CH_3CN$ . Since the stratospheric budget

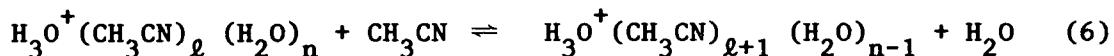


TABLE 1 : Chemical scheme for the positive ions in the stratosphere and adopted rate constants (X = CH<sub>3</sub>CN).

Reaction	Rate constant (in cm <sup>3</sup> s <sup>-1</sup> for 2-body reactions and in cm <sup>6</sup> s <sup>-1</sup> for 3-body reactions)
$O_2^+ + O_2 + M \rightarrow O_4^+ + M$	$k_1 = 2.6 \times 10^{-30} (300/T)^{3.2}$
$O_4^+ + M \rightarrow O_2^+ + O_2 + M$	$k_{1b} = 2.4 \times 10^{-6} (300/T) e^{-4900/T}$
$O_4^+ + O_3 \rightarrow O_5^+ + O_2$	$k_2 = 1 \times 10^{-10}$
$O_5^+ + O_2 \rightarrow O_4^+ + O_3$	$k_{2b} = k_2/2 \times 10^4$
$O_5^+ + H_2O \rightarrow O_2^+ \cdot H_2O + O_3$	$k_3 = 1.2 \times 10^{-9}$
$O_4^+ + H_2O \rightarrow O_2^+ \cdot H_2O + O_2$	$k_4 = 1.5 \times 10^{-9}$
$O_2^+ \cdot H_2O + O_2 \rightarrow O_4^+ + H_2O$	$k_{4b} = 2 \times 10^{-10} e^{-2300/T}$
$O_2^+ \cdot H_2O + H_2O \rightarrow H_3O^+ + OH + O_2$	$k_5 = 2.4 \times 10^{-10}$
$O_2^+ \cdot H_2O + H_2O \rightarrow H_3O^+ \cdot OH + O_2$	$k_6 = 1.2 \times 10^{-9}$
$H_3O^+ \cdot OH + H_2O \rightarrow H_3O^+ \cdot H_2O + OH$	$k_7 = 1.4 \times 10^{-9}$
$H_3O^+ + N_2O_5 \rightarrow NO_2^+ \cdot H_2O + HNO_3$	$k_8 = 1.3 \times 10^{-9}$
$H_3O^+ + HNO_3 \rightarrow NO_2^+ \cdot H_2O + H_2O$	$k_9 = 1.6 \times 10^{-9}$
$NO_2^+ \cdot H_2O + H_2O + M \rightarrow NO_2^+ (H_2O)_2 + M$	$k_{10} = 2 \times 10^{-27}$
$NO_2^+ (H_2O)_2 + H_2O \rightarrow H_3O^+ \cdot H_2O + HNO_3$	$k_{11} = 2 \times 10^{-10}$
$H_3O^+ + H_2O + M \rightarrow H_3O^+ \cdot H_2O + M$	$k_{12} = 2.5 \times 10^{-17} T^{-4}$
$H_3O^+ \cdot H_2O + M \rightarrow H_3O^+ + H_2O + M$	$k_{12b} = 3.77 \times 10^{10} T^{-5} e^{-15910/T}$
$H_3O^+ \cdot H_2O + H_2O + M \rightarrow H_3O^+ (H_2O)_2 + M$	$k_{14} = 2.8 \times 10^{-8.1} T^{-7.5}$
$H_3O^+ (H_2O)_2 + M \rightarrow H_3O^+ \cdot H_2O + H_2O + M$	$k_{14b} = 1.14 \times 10^{18.9} T^{-8.5} e^{-9819/T}$
$H_3O^+ (H_2O)_2 + H_2O + M \rightarrow H_3O^+ (H_2O)_3 + M$	$k_{17} = 2.9 \times 10^{-7} T^{-8.1}$
$H_3O^+ (H_2O)_3 + M \rightarrow H_3O^+ (H_2O)_2 + H_2O + M$	$k_{17b} = 3.44 \times 10^{21} T^{-9.1} e^{-9013/T}$
$H_3O^+ (H_2O)_3 + H_2O + M \rightarrow H_3O^+ (H_2O)_4 + M$	$k_{18} = 1.52 \times 10^7 T^{-14}$
$H_3O^+ (H_2O)_4 + M \rightarrow H_3O^+ (H_2O) + H_2O + M$	$k_{18b} = 1.51 \times 10^{34} T^{-15} e^{-6394/T}$
$H_3O^+ (H_2O) + X \rightarrow H_3O^+ (H_2O)X + H_2O$	$k_{20} = 3.6 \times 10^{-9}$
$H_3O^+ \cdot H_2O \cdot X + H_2O \rightarrow H_3O^+ (H_2O)_2 + X$	$k_{20b} = 0$ (case 1) = $3.5 \times 10^{-16}$ (case 2)

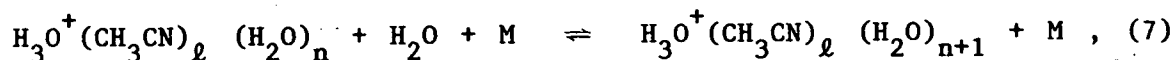


of methanol is not yet known, the possible effect of a Y molecule has not been considered in the model. The general PH to NPH conversion will therefore be written



for  $\ell \geq 0$  and  $n \geq 1$ . Smith et al (1981) have measured the rate of such reactions for  $\ell = 0$ . They obtain rather high values showing that, even with a small ambient concentration of acetonitrile, the conversion from PH to NPH could be very efficient. In principle, however, this process could be limited by a reconversion of NPH to PH whose amplitude depends on the corresponding reverse reactions rates. Since the value of these latter constants is not known, two extreme cases have been considered in the calculation : case 1 assumes that the reverse rate constant is equal to zero for reactions 20, 22, 24, 27, 29, 31 and 34 - see table 1 and fig. 1. In case 2, reverse reactions are assumed to be efficient with the corresponding rates as given in table 1. In order to fit the observation at 35 km, the model requires in each case a different acetonitrile profile. The concentration value as assumed in case 1 is uniformly multiplied by 50 when case 2 is considered (fig. 2). The shape of these profiles is based on an analysis by Henschen and Arnold (1981). Reactions for  $\ell > 0$  have never been measured and it is therefore assumed that  $k_{27} = k_{20}/5$ ;  $k_{34} = k_{29} = k_{22}$ ;  $k_{31} = k_{24}$ .

Hydration of the NPH ions must also be considered. Several equilibrium constants of the following reactions



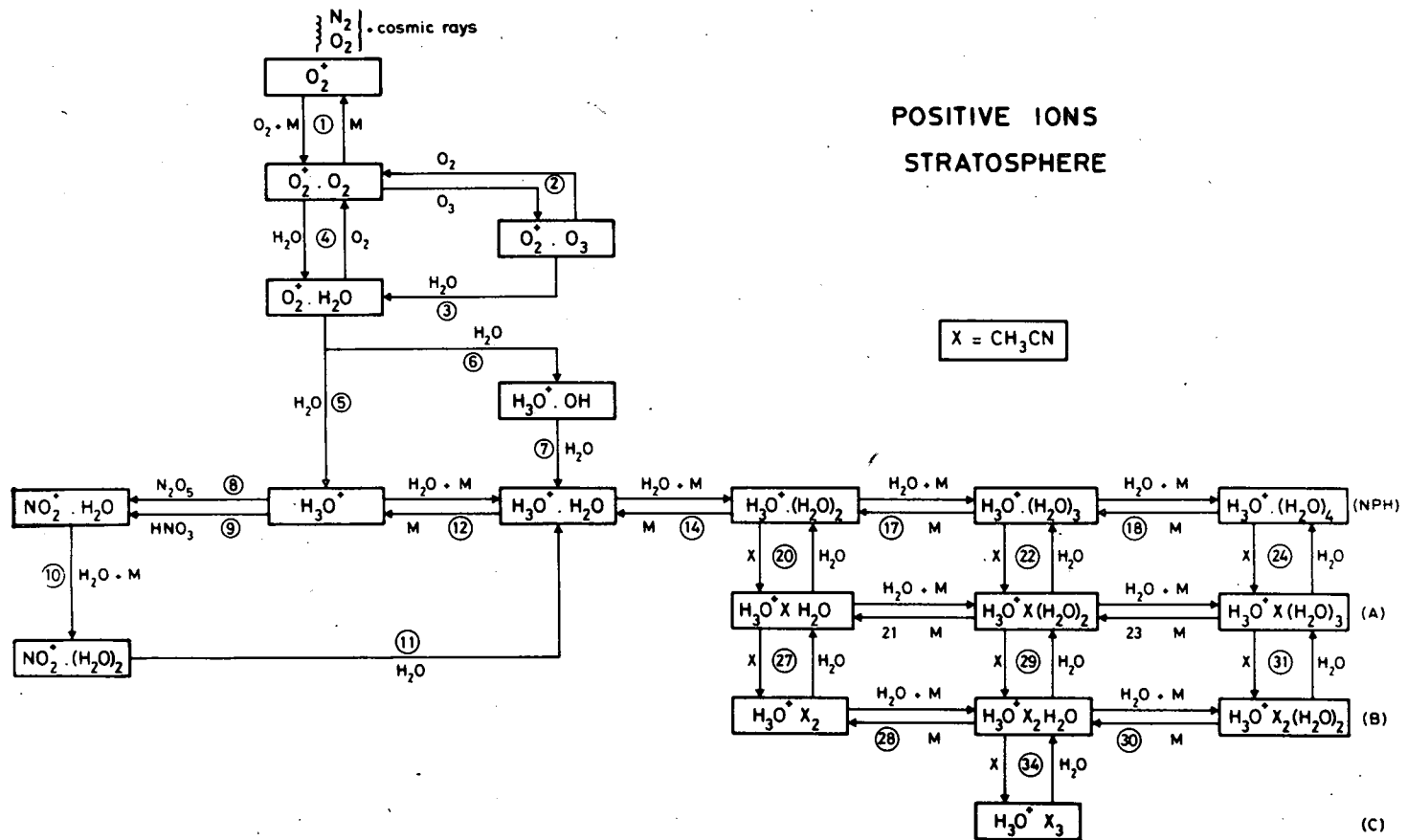


Fig. 1.- Chemical scheme adopted for the positive ions in the stratosphere.

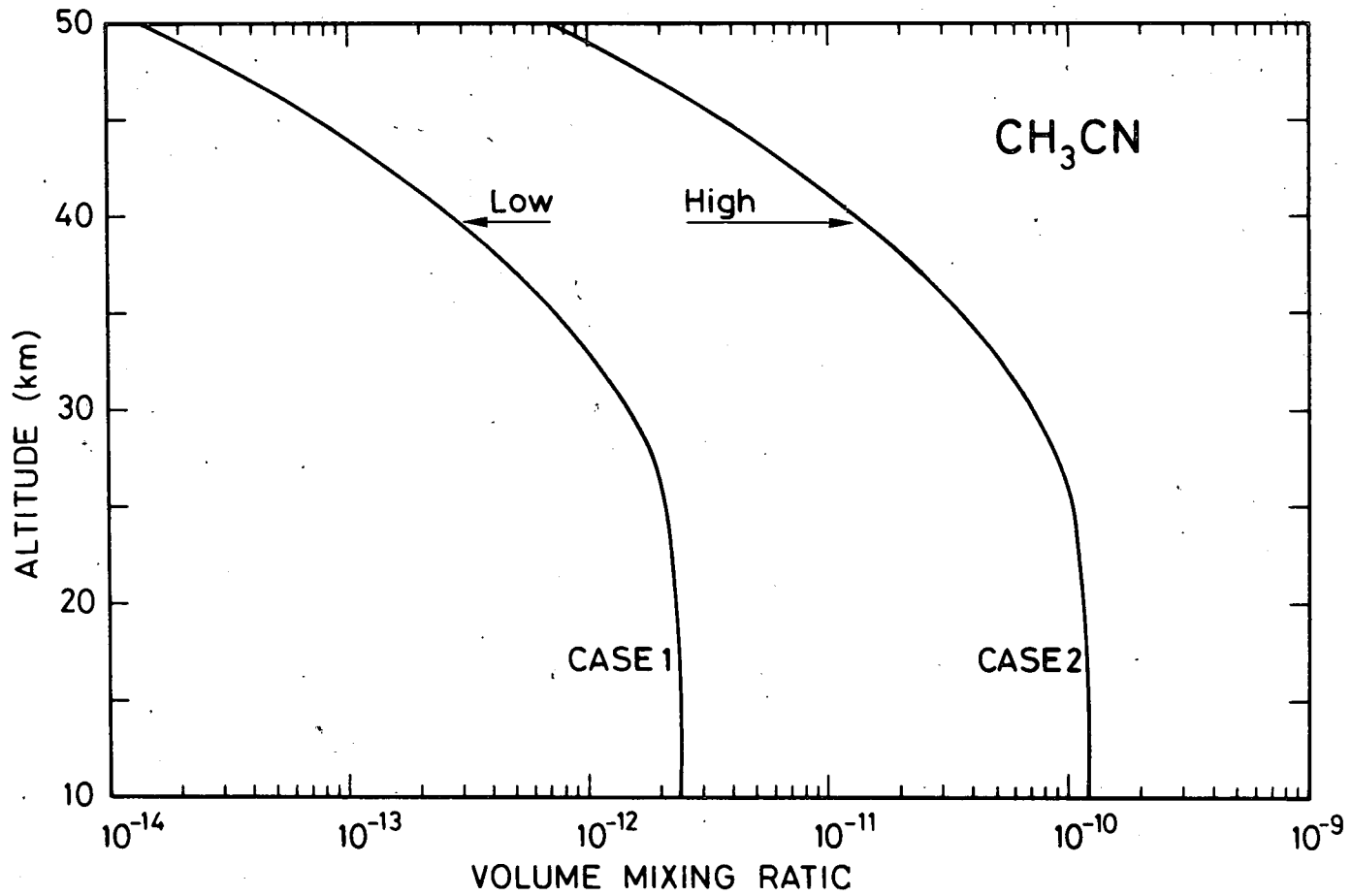


Fig. 2.- Vertical distributions of the acetonitrile mixing ratio adopted in the model.

have been measured by Böhringen and Arnold (1981) at the specific temperature of 227 K. Since the value of these constants depends crucially on the local temperature, and in order to introduce in the model such a dependence, it has been assumed that the  $\Delta S$  value corresponding to these reactions is equal to  $-24 \text{ cal K}^{-1} \text{ mol}^{-1}$ . In fact, this parameter does not change considerably from one reaction to another and for example in the processes considered by Lau et al (1982),  $\Delta S$  varies only from  $-21.7$  to  $-28.4 \text{ cal K}^{-1} \text{ mol}^{-1}$ .

Using the measured  $K_{\text{eq}}$  value at 227 K and the assumed  $\Delta S$  value, the equilibrium constant is derived from the formulae

$$K_{\text{eq}}(\text{atm}^{-1}) = e^{\Delta S/R} e^{-\Delta H/RT} \quad (8)$$

$$K_{\text{eq}}(\text{cm}^3) = 1.367 \times 10^{-22} T K (\text{atm}^{-1}) \quad (8\text{bis})$$

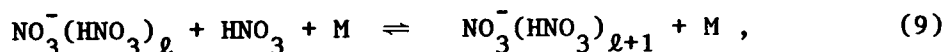
where  $R$  is the gas constant,  $\Delta H$  and  $\Delta S$  the difference of enthalpy and entropy for the reaction which is considered. The determination of the thermodynamical parameters requires detailed laboratory work as recently started by Arnold and Böhringer (private communication). In the expectation of measured values of forward reaction rates for processes (7) the following working values are introduced in the model (see table 1):  $k_{28} = k_{21} = k_{17}$  and  $k_{30} = k_{23} = k_{18}$ . Such an assumption is quite acceptable since the concentration values depend essentially on the specified equilibrium constants and not on the individual forward and reverse reaction rates.

The numerous rate constants used in the model will not be discussed in this paper. Most values listed in table 1 are taken from the paper by Albritton (1978) in which the most important references are quoted. In some cases when the reaction rate or its temperature

dependence is not known the value indicated in the table refers to the assumption which is made.

## 2.2. Negative ions

The negative ion scheme which applies to the stratosphere is very complicated. The starting point is the attachment of a free electron on an oxygen molecule.  $O_2^-$  is subsequently transformed into  $CO_3^-$  through different paths (see Ferguson, 1979) and  $CO_3^-$  is then converted into  $NO_3^-$ . This latter ion is particularly stable since its electron affinity is one of the highest of all known ions. Clustering reactions are however possible, essentially with water vapor and nitric acid, leading to heavy ions such as  $NO_3^-(HNO_3)_\ell (H_2O)_n$  with  $\ell$  and  $n \geq 0$ . Since these ions react rapidly with sulfuric acid (Viggiano et al, 1980), clusters of type  $HSO_4^-(HNO_3)_\ell (H_2SO_4)_m (H_2O)_n$  are expected to appear and can be identified from mass spectroscopic observations (see e.g. the latest papers by Arijs et al (1982) and Arnold et al (1982)). Figure 3 shows a possible reaction scheme suggested by Arijs et al (1981) to explain his observational data. Most of the corresponding kinetics is unknown except reaction rates  $k_{49}$ ,  $k_{60}$  and  $k_{64}$  (see table 2) which have been recently measured by Viggiano et al (1982). In most cases, working values have thus been adopted. For reactions of type



no rate constant is available except for  $\ell = 0$ , where Fehsenfeld et al indicate a value slightly larger than  $1 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1}$ . Therefore, a forward rate constant of  $1 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1}$  has been applied for all values of  $\ell$  with an equilibrium constant taken from the study by Davidson et al (1977) and Wlodek et al (1980). The hydration

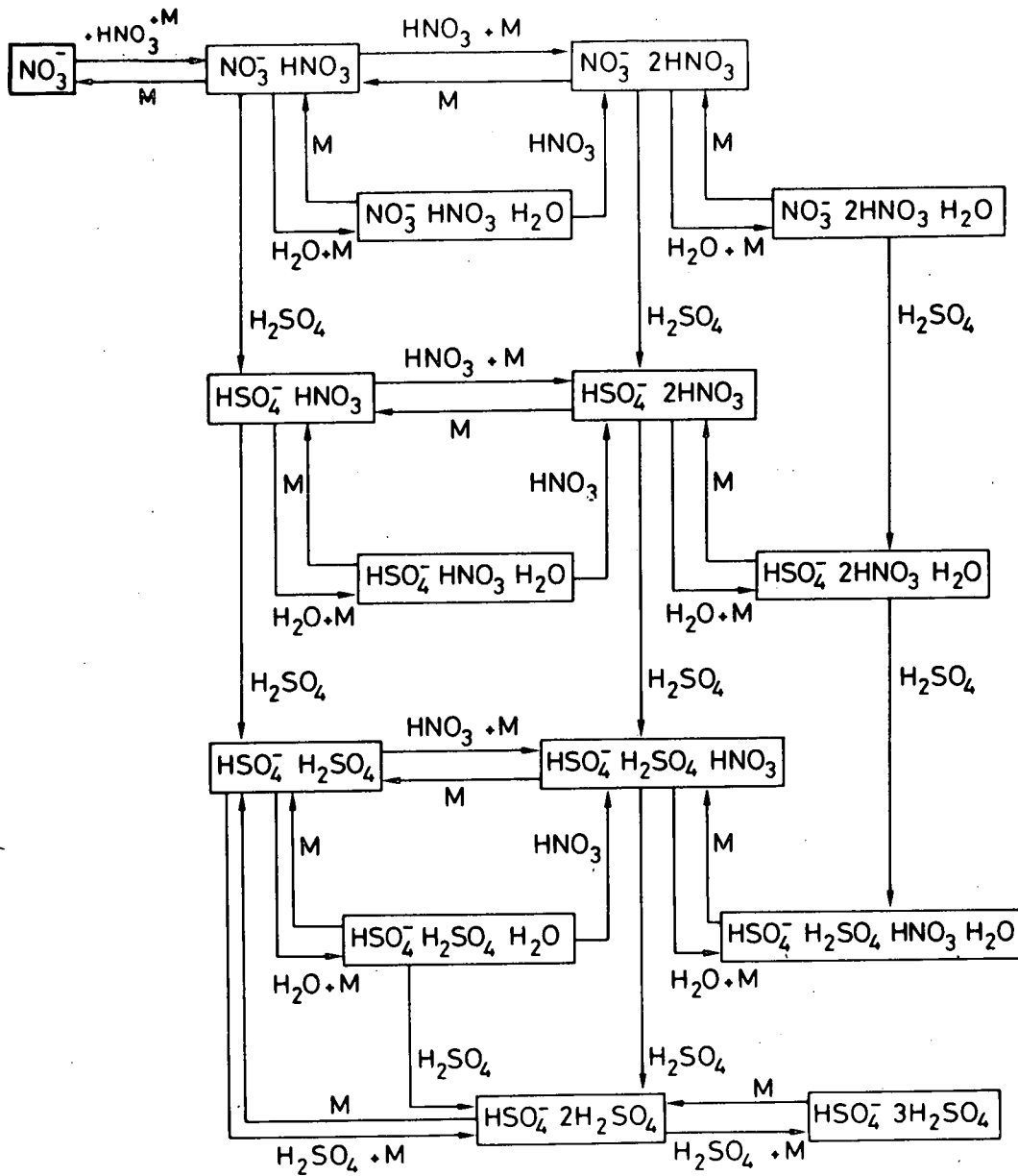
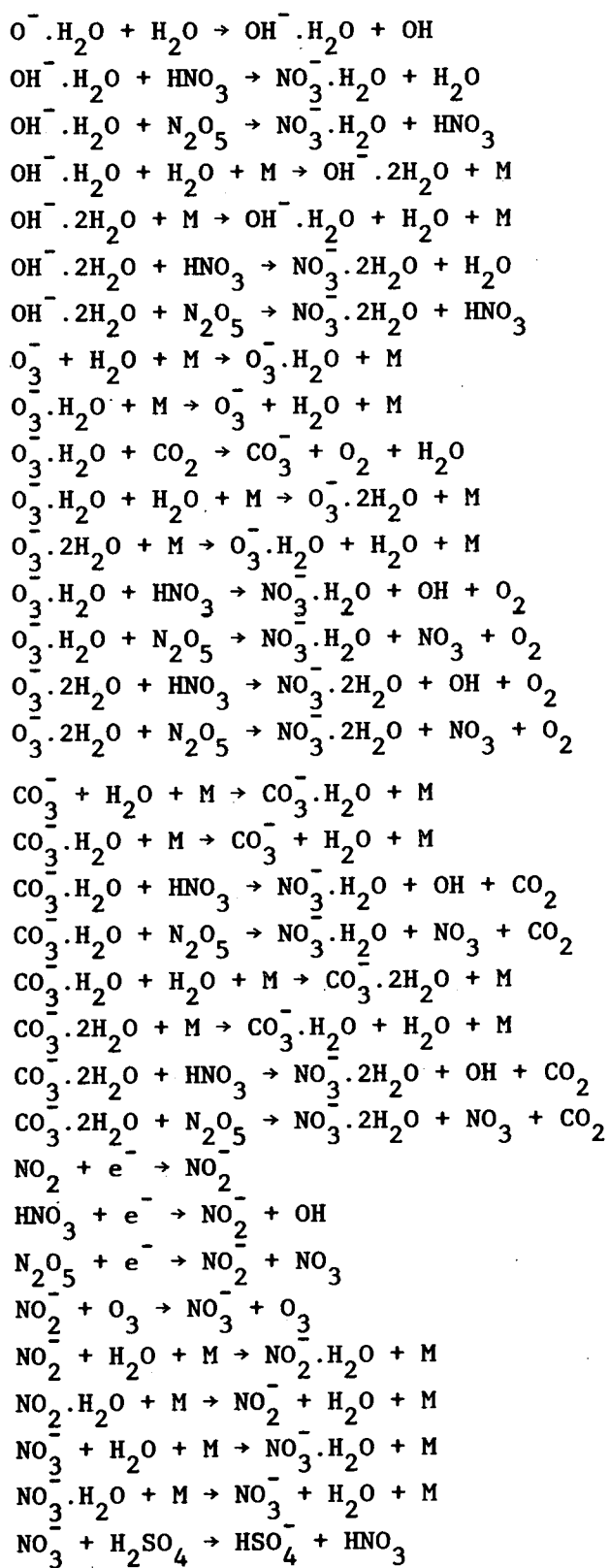


Fig. 3.- Chemical scheme related to the most abundant negative ions in the stratosphere (Adapted from Arijs et al, 1981).

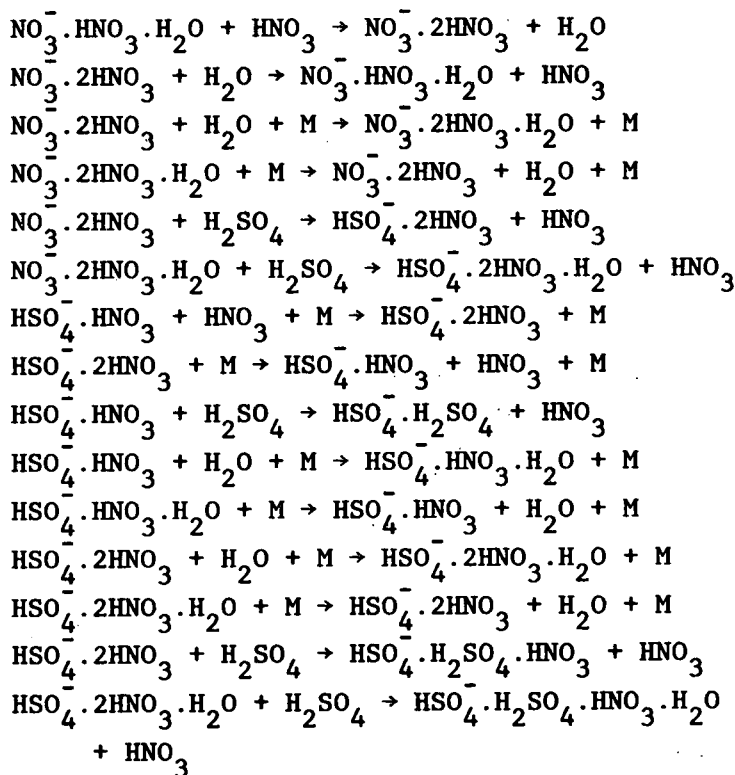
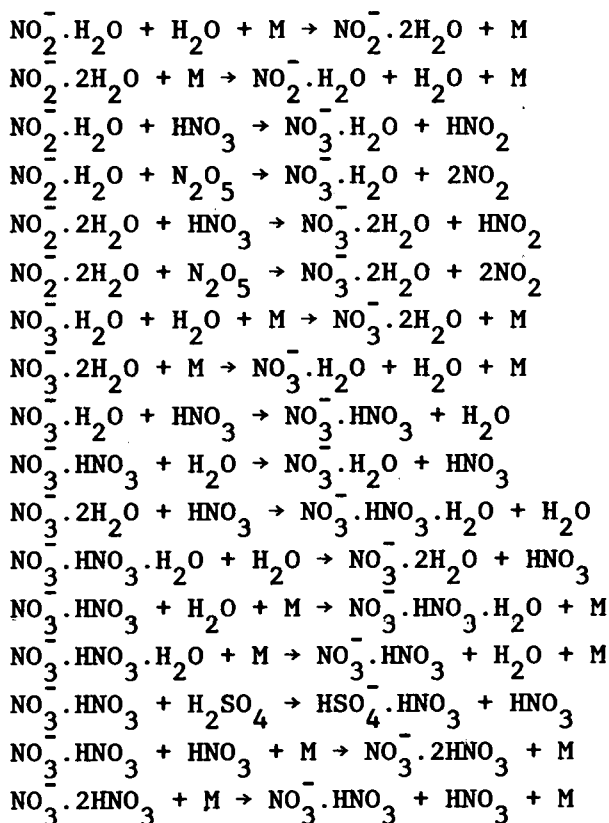


TABLE 2 : Chemical scheme for the negative ion in the stratosphere and adopted rate constants.

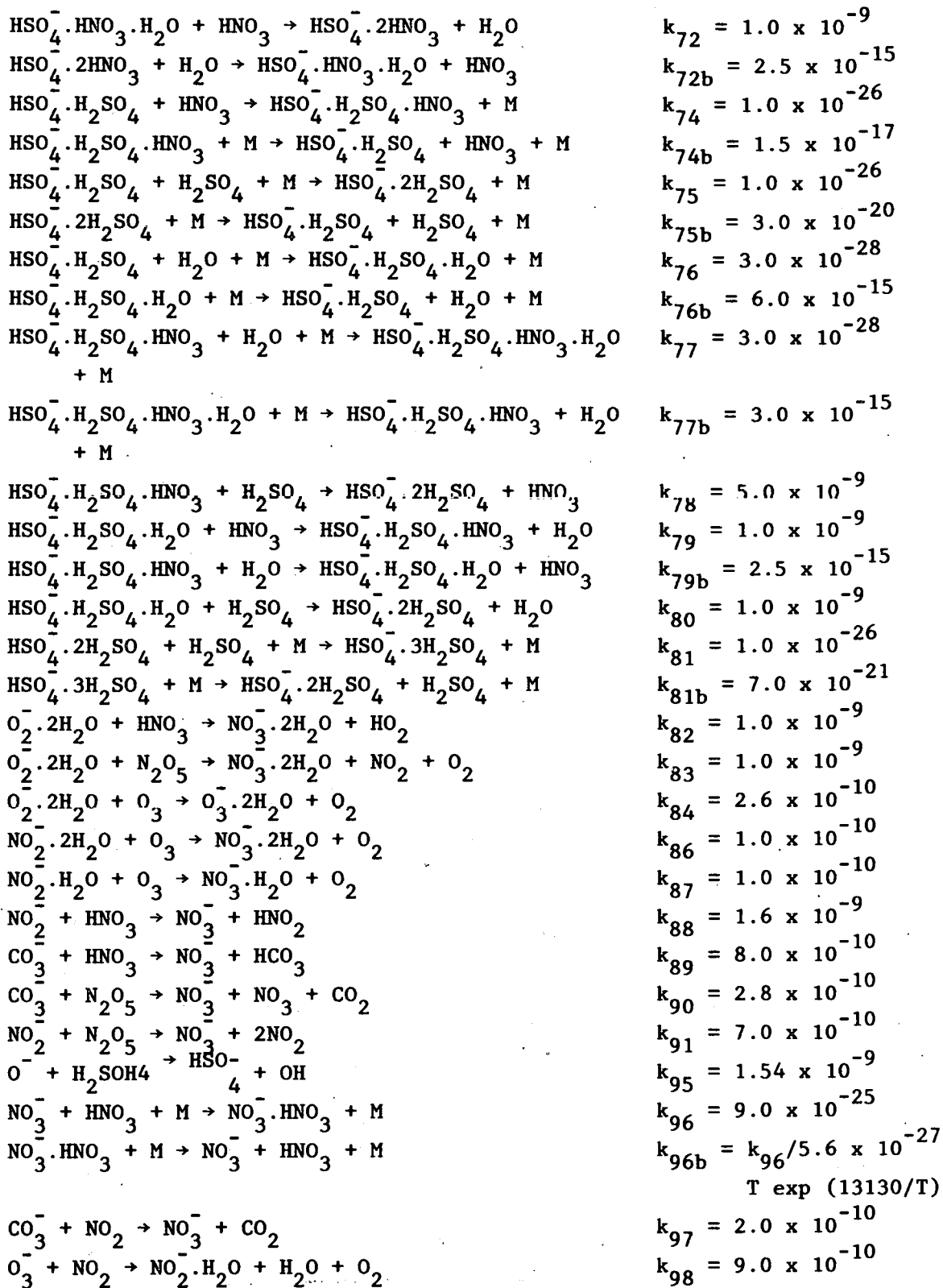
Reaction	Rate constant (in $\text{cm}^3 \text{s}^{-1}$ for 2-body reactions and in $\text{cm}^6 \text{s}^{-1}$ for 3-body reactions)
$e^- + O_2 + M \rightarrow O_2^- + M$	$k_1 = 2 \times 10^{-30}$
$O_2^- + O_3 \rightarrow O_3^- + O_2$	$k_2 = 6 \times 10^{-10}$
$O_3^- + CO_2 \rightarrow CO_3^- + O_2$	$k_3 = 5.3 \times 10^{-10}$
$CO_3^- + O_2 \rightarrow O_3^- + CO_2$	$k_{3b} = 3.9 \times 10^{-15}$
$O_2^- + O_2 + M \rightarrow O_4^- + M$	$k_4 = 3.4 \times 10^{-31}$
$O_4^- + M \rightarrow O_2^- + O_2 + M$	$k_{4b} = 2.7 \times 10^{-14}$
$O_4^- + CO_2 \rightarrow CO_4^- + O_2$	$k_5 = 4.3 \times 10^{-10}$
$CO_4^- + O_2 \rightarrow O_4^- + CO_2$	$k_{5b} = 2 \times 10^{-13}$
$CO_4^- + O_3 \rightarrow O_3^- + CO_2 + O_2$	$k_6 = 1.3 \times 10^{-10}$
$CO_4^- + H_2O \rightarrow O_2^- \cdot H_2O + CO_2$	$k_7 = 1.3 \times 10^{-9}$
$O_2^- \cdot H_2O \rightarrow CO_4^- + H_2O$	$k_{7b} = 5.8 \times 10^{-10}$
$O_2^- + H_2O + M \rightarrow O_2^- \cdot H_2O + M$	$k_9 = 2.2 \times 10^{-28}$
$O_2^- \cdot H_2O + M \rightarrow O_2^- + H_2O + M$	$k_{9b} = k_9 / 1.0 \times 10^{-14}$
$O_2^- \cdot H_2O + NO_2 \rightarrow NO_2^- + O_2 + H_2O$	$k_{10} = 9.0 \times 10^{-10}$
$O_2^- \cdot H_2O + H_2O + M \rightarrow O_2^- \cdot 2H_2O + M$	$k_{11} = 6.0 \times 10^{-28}$
$O_2^- \cdot 2H_2O + M \rightarrow O_2^- \cdot H_2O + H_2O + M$	$k_{11b} = k_{11} / 3 \times 10^{-16}$
$O_2^- \cdot H_2O + O_3 \rightarrow O_3^- \cdot H_2O + O_2$	$k_{13} = 2.3 \times 10^{-10}$
$O_2^- \cdot H_2O + HNO_3 \rightarrow NO_3^- \cdot H_2O + HO_2$	$k_{14} = 1.0 \times 10^{-9}$
$O_2^- \cdot H_2O + N_2O_5 \rightarrow NO_3^- \cdot H_2O + NO_2 + O_2$	$k_{15} = 1.0 \times 10^{-9}$
$O_3 + e^- \rightarrow O^- + O_2$	$k_{16} = 9.1 \times 10^{-12} (T/300)^{1.46}$
$O^- + O_2 \rightarrow O_3 + e^-$	$k_{16b} = 1.0 \times 10^{-12}$
$O^- + O_3 \rightarrow O_3^- + O$	$k_{17} = 8.0 \times 10^{-10}$
$O^- + H_2O + M \rightarrow O^- \cdot H_2O + M$	$k_{19} = 1.3 \times 10^{-28}$
$O^- \cdot H_2O + HNO_3 \rightarrow NO_3^- \cdot H_2O + OH$	$k_{20} = 1.0 \times 10^{-9}$
$O^- \cdot H_2O + N_2O_5 \rightarrow NO_3^- \cdot H_2O + HNO_2$	$k_{21} = 1.0 \times 10^{-9}$

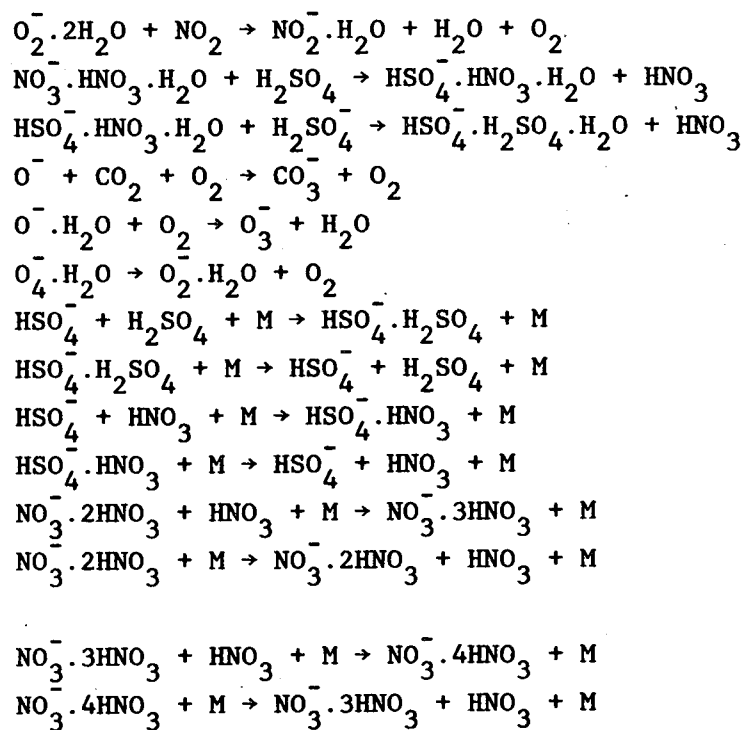


$$\begin{aligned}
k_{22} &= 1.0 \times 10^{-11} \\
k_{23} &= 1.0 \times 10^{-9} \\
k_{24} &= 1.0 \times 10^{-9} \\
k_{25} &= 3.5 \times 10^{-28} \\
k_{25b} &= k_{25}/10^{-14} \\
k_{26} &= 1.0 \times 10^{-9} \\
k_{27} &= 1.0 \times 10^{-9} \\
k_{28} &= 2.7 \times 10^{-28} \\
k_{28b} &= k_{28}/10^{-14} \\
k_{30} &= 3.5 \times 10^{-10} \\
k_{31} &= 5.0 \times 10^{-28} \\
k_{31b} &= k_{31}/10^{-14} \\
k_{33} &= 1.0 \times 10^{-9} \\
k_{34} &= 1.0 \times 10^{-9} \\
k_{35} &= 1.0 \times 10^{-9} \\
k_{36} &= 1.0 \times 10^{-9} \\
k_{37} &= 1 \times 10^{-28} \\
k_{37b} &= 3.3 \times 10^{-14} \\
k_{38} &= 1.0 \times 10^{-9} \\
k_{39} &= 1.0 \times 10^{-9} \\
k_{40} &= 5.0 \times 10^{-28} \\
k_{40b} &= k_{40}/6.0 \times 10^{-17} \\
k_{41} &= 1.0 \times 10^{-9} \\
k_{42} &= 1.0 \times 10^{-9} \\
k_{43} &= 5.0 \times 10^{-8} \\
k_{44} &= 5.0 \times 10^{-8} \\
k_{45} &= 5.0 \times 10^{-8} \\
k_{46} &= 1.2 \times 10^{-10} \\
k_{47} &= 1.6 \times 10^{-28} \\
k_{47b} &= 5.0 \times 10^{-15} \\
k_{48} &= 1.6 \times 10^{-28} \\
k_{48b} &= k_{48}/4.4 \times 10^{-15} \\
k_{49} &= 2.6 \times 10^{-9}
\end{aligned}$$

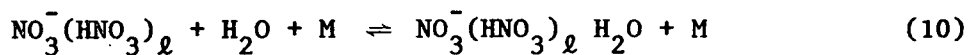


$$\begin{aligned}
k_{51} &= 1.6 \times 10^{-28} \\
k_{51b} &= k_{51}/8.0 \times 10^{-16} \\
k_{52} &= 1.0 \times 10^{-9} \\
k_{53} &= 1.0 \times 10^{-9} \\
k_{54} &= 1.0 \times 10^{-9} \\
k_{55} &= 1.0 \times 10^{-9} \\
k_{56} &= 1.6 \times 10^{-28} \\
k_{56b} &= k_{56}/1.96 \times 10^{-16} \\
k_{57} &= 3.0 \times 10^{-9} \\
k_{57b} &= k_{57}/6.0 \times 10^5 \\
k_{58} &= 1.0 \times 10^{-9} \\
k_{58b} &= k_{58}/2.0 \times 10^5 \\
k_{59} &= 3 \times 10^{-28} \\
k_{59b} &= 6.0 \times 10^{-15} \\
k_{60} &= 2.3 \times 10^{-9} \\
k_{61} &= 1.0 \times 10^{-26} \\
k_{61b} &= k_{61}/1.94 \times 10^{-27} T \\
&\quad \exp(9240/T) \\
k_{62} &= 1.0 \times 10^{-9} \\
k_{62b} &= k_{62}/2.0 \times 10^5 \\
k_{63} &= 3.0 \times 10^{-28} \\
k_{63b} &= 3.0 \times 10^{-15} \\
k_{64} &= 1.1 \times 10^{-9} \\
k_{65} &= 4.0 \times 10^{-10} \\
k_{66} &= 1.0 \times 10^{-26} \\
k_{66b} &= 5.0 \times 10^{-18} \\
k_{67} &= 5.0 \times 10^{-10} \\
k_{68} &= 3.0 \times 10^{-28} \\
k_{68b} &= 6.0 \times 10^{-15} \\
k_{69} &= 3.0 \times 10^{-28} \\
k_{69b} &= 3.0 \times 10^{-15} \\
k_{70} &= 5.0 \times 10^{-10} \\
k_{71} &= 1.0 \times 10^{-9}
\end{aligned}$$



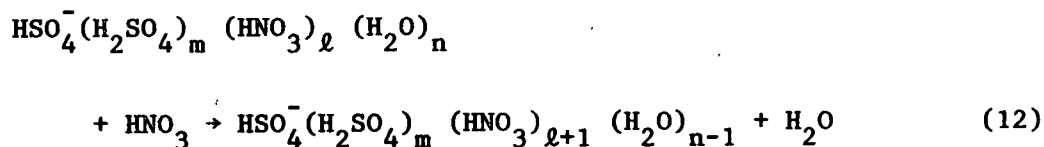
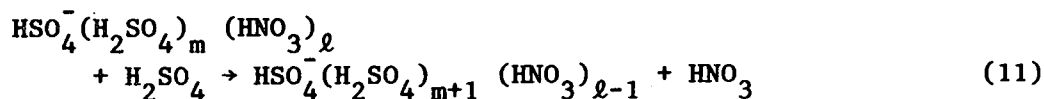


$$\begin{aligned}
k_{99} &= 9.0 \times 10^{-10} \\
k_{100} &= 1.0 \times 10^{-9} \\
k_{101} &= 1.0 \times 10^{-9} \\
k_{102} &= 3.1 \times 10^{-28} \\
k_{103} &= 1.0 \times 10^{-11} \\
k_{106} &= 1.0 \times 10^{-10} \\
k_{150} &= 3.0 \times 10^{-26} \\
k_{150b} &= 1.0 \times 10^{-21} \\
k_{151} &= 2.0 \times 10^{-26} \\
k_{151b} &= 1.0 \times 10^{-21} \\
k_{152} &= 1.0 \times 10^{-26} \\
k_{152b} &= k_{152} / 6.26 \times 10^{-29} \\
&\quad T \exp(7070/T) \\
k_{153} &= 1.0 \times 10^{-26} \\
k_{153b} &= k_{153} / 5.91 \times 10^{-27} \\
&\quad T \exp(4696/T)
\end{aligned}$$



has been assumed to be slower with a rate constant of  $3 \times 10^{-28} \text{ cm}^6 \text{ s}^{-1}$ . Since the equilibrium constant related to this process is unknown, an adjustment of this parameter has been made. The error in relation to this uncertainty is small since most of the calculated concentrations are not very sensitive to these reactions.

The rate constants of the following two-body reactions, namely



have been put equal to  $1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . The same value has been used for the rates referring to all reactions of  $\text{HNO}_3$  and  $\text{N}_2\text{O}_5$  with negative cluster ions. All other rate constants have been taken from the compilation by Albritton (1978) or, in certain cases when no data is available, have been estimated rather arbitrarily or adjusted to fit the observation at 35 km. The adopted values are given in table 2.

### 3. MODEL DESCRIPTION

Since the lifetime of all ions is very short, equilibrium conditions are reached almost instantaneously. Therefore the system

describing the balance of each ionic species is purely algebraic and can be written for the positive and the negative ions respectively by the equation

$$A X = B \quad (13)$$

when  $X$  is a column vector representing the concentration values  $x_j$  ( $j = 1$  to  $N$ , where  $N$  is the number of species),  $B$  with elements  $b_i$  ( $i = 1$  to  $N$ ) represents the external sources of ionization and depends therefore on the value of  $Q$  and  $A$  is a  $N \times N$  square matrix whose elements  $a_{ij}$  take into account all chemical processes. These factors which represent the inverse of the time constant associated to reaction from ion  $j$  to ion  $i$ , are a function of the chemical rate constants and of the neutral species concentrations. In the case of the diagonal elements  $a_{ii}$  which represent the loss term of ion  $i$ , a term accounting for the recombination between positive and negative charges appears. Assuming that the value of the recombination rates are identical for all ions (eq. 3) and introducing the electroneutrality condition, the  $a_{ii}$  coefficients for the positive ions become independent of the concentration of the negative ions and vice versa but dependent on the  $Q$  value through equation (4).

The two decoupled algebraic systems are then solved by a classical inversion method. For the positive charges, the model takes into account 25 different species and 44 chemical reactions while for the negative charges 38 different species and 134 chemical reactions are considered. The concentration values of the neutral trace species are taken from the 1-D model described by Brasseur et al (1982) except for sulfuric acid whose vertical profile is similar to that given by the model of Turco et al (1979). The vertical distribution of the temperature is taken from the US Standard Atmosphere (1966).

## 4. MODEL RESULTS

### 4.1. Positive ions

When the concentration values or the relative abundance of the positive ions provided by the model are analyzed, it immediately appears that the conditions are rapidly changing with the altitude level. This has to be attributed to the strong dependence of the equilibrium values to the local temperature. The analysis of any observational data therefore requires a very accurate knowledge of the temperature in addition to the water vapor concentration. The amount of  $\text{CH}_3\text{CN}$  which is present is also an important parameter but no observation is yet available. From the model calculation, it can however be deduced, when case 1 (low  $\text{CH}_3\text{CN}$  and no NPH to PH reversion) is compared to case 2 (high  $\text{CH}_3\text{CN}$  and an efficient NPH to PH reversion) that the observations at all altitude are much better fitted when case 1 is adopted. In other words, as suggested by figure 4, the reactions converting proton hydrates into non-proton hydrates should be very efficient even at low level where the water vapor concentration is relatively high. The reverse mechanism can therefore probably be neglected in the whole stratosphere.

One can show easily that the reversion of NPH to PH will occur only if the reverse reaction rate becomes of the order of  $\alpha[n^-]/[\text{H}_2\text{O}]$  where  $\alpha$  is the recombination coefficient,  $[n^-]$  the total ion concentration and  $[\text{H}_2\text{O}]$  the water vapor concentration. When the parameters, temperature and concentrations values adopted in the present model are used, the reversion reaction becomes efficient for a rate larger than  $1 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ .

Arnold et al (1981a) have divided the NPH ions into three categories called A, B and C. A refers to ions with  $\text{H}^+\text{X}$  cores, B to



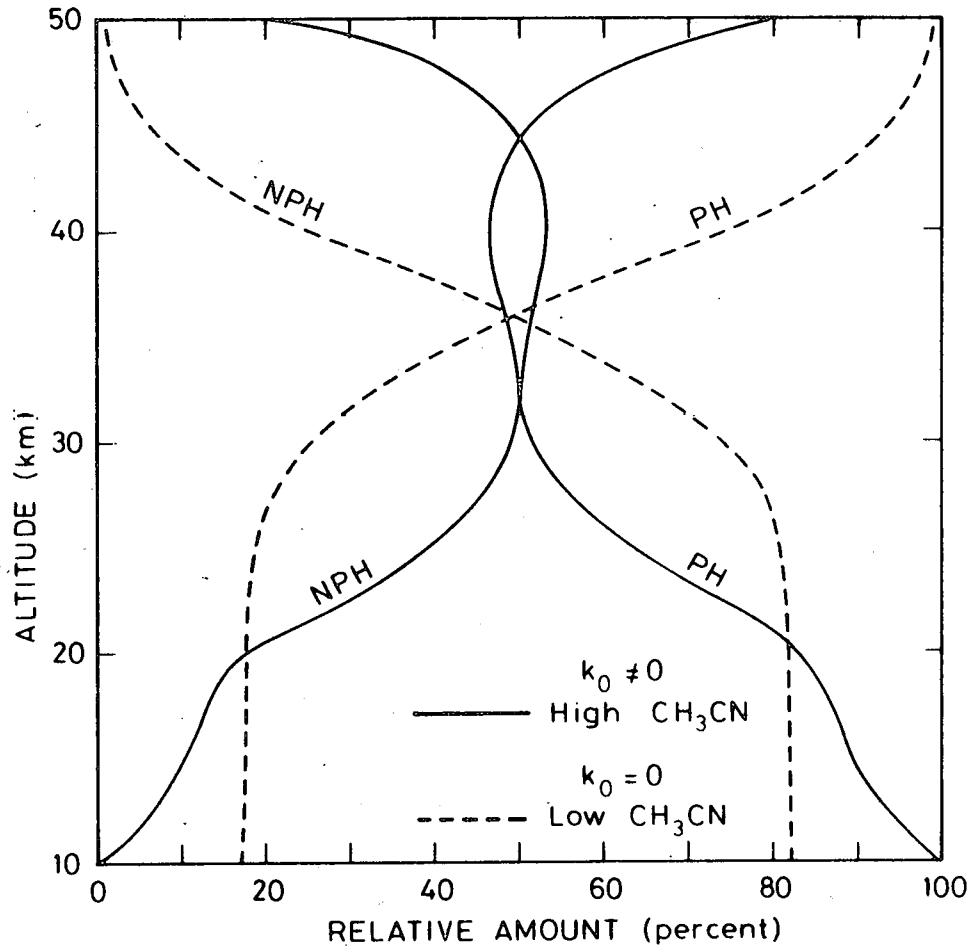


Fig. 4.- Relative amount of the proton hydrates and the non proton hydrates calculated for two different conditions (cases 1 and 2).

ions with  $H^+X_2$  cores and C to ions with  $H^+X_3$  cores. Table 3 shows the abundance of these three subfamilies and of the NPH as given by the model and by several observations. Given the large dispersion of the data, the theoretical results can be considered as satisfactory except maybe for the C group for which the model overestimates the relative amount. Table 3 also provides the values of  $R_1$ ,  $R_2$  and  $R_3$  ratios which have been defined by Arnold et al (1981a) as follows

$$R_1 = \frac{[NPH]}{[PH]} = \frac{[A] + [B] + [C]}{[PH]} = \frac{k_1 [CH_3CN]}{\alpha [n^-]}$$

$$R_2 = \frac{[B] + [C]}{[A]} = \frac{k_2 [CH_3CN]}{\alpha [n^-]}$$

$$R_3 = \frac{[C]}{[B]} = \frac{k_3 [CH_3CN]}{\alpha [n^-]}$$

When writing the right-hand terms in these ratios, it is assumed that no reverse reaction from C to B, B to A and A to PH occurs.  $k_1$ ,  $k_2$  and  $k_3$  are the effective conversion rate from one category to the other. Since these constants have the same order of magnitude ( $\sim 3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ), one would expect to have  $R_1 \cong R_2 \cong R_3$ .

The model as the observation by Arnold et al (1981a) indicate that indeed  $R_1 \cong R_2$  (which confirms that in this case the reconversion from NPH to PH is slow or can even be neglected). The measurements by Arijs et al (1982) made at higher temperature provide values of  $R_2$  which are smaller than  $R_1$ , suggesting that reverse reactions of B to A become active with increasing temperature. At 35 km (and above)  $R_3$  appears to be considerably smaller than  $R_1$  and  $R_2$ . Arnold et al (1981a) have concluded that a reverse reaction from C to B is probably

TABLE 3 : Concentration of the NPH ions belonging to the A, B and C subfamilies (expressed in percent relative to the total ion density), and  $R_1$ ,  $R_2$  and  $R_3$  ratios (see text for explanation).

	Observation (35 km)				
	Arijs <u>et al</u> (1982a)		Arnold <u>et al</u>	Model	
	Sept. 80	June 80	(1981a)	35 km	25 km
[A]	37.1	53.7	26	27.6	14.6
[B]	13.5	8.4	31	19.1	12.8
[C]	2.5	-	3	7.6	53.3
$R_1$	1.15	1.64	1.54	1.30	4.2
$R_2$	0.43	0.157	1.27	0.97	4.5
$R_3$	0.18	-	0.1	0.4	4.2

is probably occurring or that a supplementary loss process for the C ions has to be considered. In fact the low  $R_3$  ratio is obtained in the model without any of these two mechanisms. The model shows that in the upper stratosphere most of the B ions happen to be  $H_3O^+(CH_3CN)_2$  ions which do not react with  $CH_3CN$  and are therefore not transformed into C ions. At lower temperatures (and therefore at lower altitude) the largest amount of B ions happen to be  $H_3O^+(CH_3CN)_2 H_2O$  ions which can be converted into C ions. As shown by table 3; the condition  $R_1 \cong R_2 \cong R_3$  is satisfied for example at 25 km. In fact, the possibility of producing C ions depends on the  $[H_3O^+X_2 H_2O] / [H_3O^+X_2]$  ratio which varies rapidly with altitude due to the strong temperature dependence of the equilibrium constant  $K_{eq}$  (28). Table 4 shows the observed and calculated abundance ratio of different hydrates at 35 km and indicates the considerable influence of the temperature on the clustering equilibrium. This explains probably the large variations between individual observations.

Figure 5 shows the relative amount of the most abundant ion species calculated by the model for case 1. According to the model results, two distinct regions can be considered : In the upper part where the proton hydrates dominate, ions with mass 55 and 73, namely  $H_3O^+(H_2O)_2$  and  $H_3O^+(H_2O)_3$  are the most abundant while below 32 km, the NPH ions, in particular with mass 141 ( $H_3O^+(CH_3CN)_3$ ) become largely dominant. Around 35 km where most observations have been made, the ions with mass 73, 78, 91, 101, 119 and 141 should be detected. If case 2 is considered, the most abundant ion in the lower stratosphere is  $H_3O^+(H_2O)_4$ , which is completely in contradiction with the reported observations.

As shown by table 5, the calculated values at 35 km are generally in good agreement with the data obtained by Arnold et al (1981a) and Arijs et al (1982a). There are some variations between individual observations which makes the comparison with the model

**TABLE 4 :** Comparison of abundance ratios obtained by the model for two temperature values and from in situ measurements.

		Observation			Model <sup>(1)</sup> (35 km)	
		Arnold <u>et al</u>	Arijs <u>et al</u> (1982)		T = 236.5 K	T = 227 K
		(1981a)	June 80	Sept. 80		
[96]/[78]	$\frac{H_3O^+X(H_2O)_2}{H_3O^+X H_2O}$	2.7	5.3	4.5	2.83	9.80
[119]/[101]	$\frac{H_3O^+X_2(H_2O)}{H_3O^+X_2}$	1.5	1.4	1.0	0.50	1.62
[91]/[73]	$\frac{H_3O^+(H_2O)_4}{H_3O^+(H_2O)_3}$	0.84	0.1	-	0.09	0.27
[114]/[96]	$\frac{H_3O^+X(H_2O)_3}{H_3O^+X(H_2O)_2}$	-	0.02	-	0.005	0.01

(1) Water vapor mixing ratio : 3.9 ppmv.

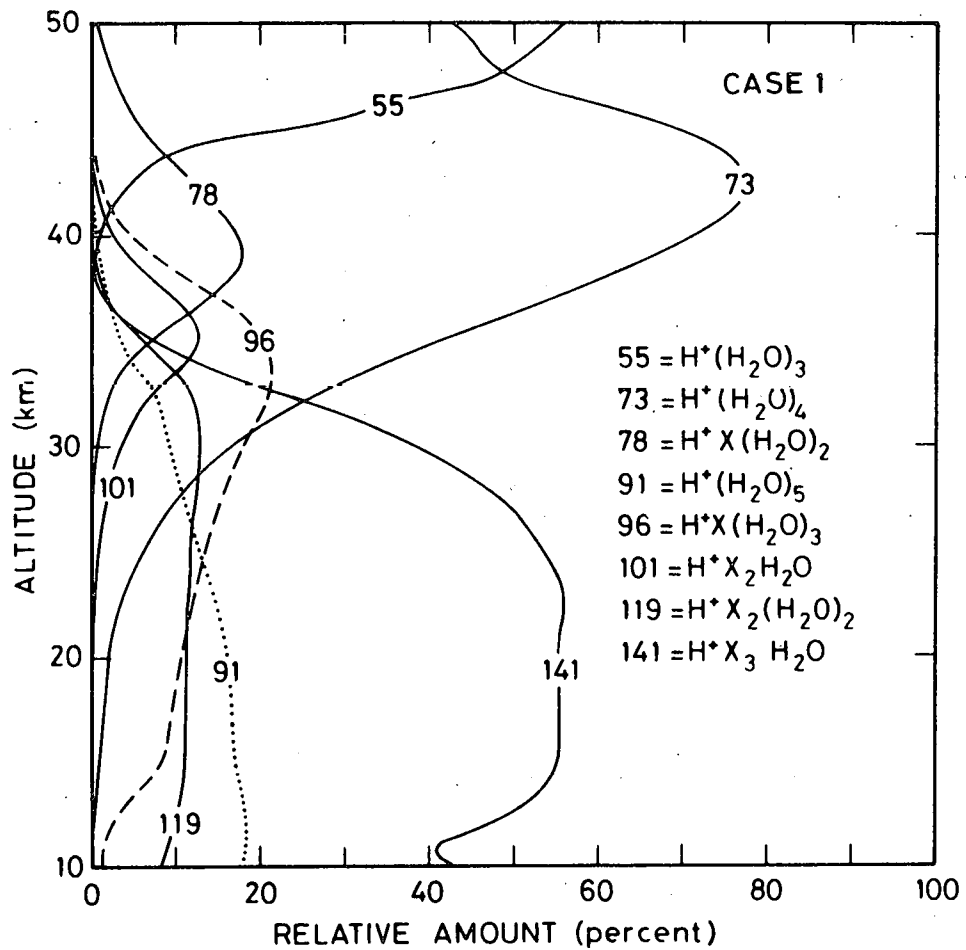


Fig. 5.- Vertical distribution of the relative amount of the most abundant positive ions in the stratosphere (case 1).

**TABLE 5 :** Comparison of calculated and observed positive ions abundances  
(in percent relative to the total ion density).

Mass	Identification X = CH <sub>3</sub> CN	Observation at ~ 35 km			Model	
		Arnold <u>et al</u> (1981a) (Nov. 77)	Arijs <u>et al</u> (1982a) (June 80)	<u>et al</u> (1982a) (Sept. 80)	(1)	(2)
55	H <sup>+</sup> (H <sub>2</sub> O) <sub>3</sub>	3.4	2.3	-	0.1	0.1
73	H <sup>+</sup> (H <sub>2</sub> O) <sub>4</sub>	21.3	32.2	38.4	41.6	44.8
78	H <sup>+</sup> X(H <sub>2</sub> O)	7.2	8.4	6.7	7.2	7.4
91	H <sup>+</sup> (H <sub>2</sub> O) <sub>5</sub>	17.8	3.4	8.5	3.7	4.0
96	H <sup>+</sup> X(H <sub>2</sub> O) <sub>3</sub>	19.6	44.4	30.4	20.4	21.1
101	H <sup>+</sup> X <sub>2</sub> H <sub>2</sub> O	10.7	3.5	6.7	12.7	13.4
119	H <sup>+</sup> X <sub>2</sub> (H <sub>2</sub> O)	16.1	4.9	6.8	6.4	6.7
136	H <sup>+</sup> X <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub>	4.4	-	-	-	-
141	H <sup>+</sup> X <sub>3</sub> H <sub>2</sub> O	2.9	-	2.5	7.6	2.2

(1) case 1 (low CH<sub>3</sub>CN ( $7 \times 10^{-13}$ ) ;  $k_r = 0$ )

(2) case 2 (high CH<sub>3</sub>CN ( $3.5 \times 10^{-11}$ ) ;  $k_r \neq 0$ ).

somewhat difficult. These changes in the successive measurements are probably explained by the differences in the state of the atmosphere (temperature, water vapor concentration, ...) and to the observation conditions (height of the gondola, error in the measurements, ...). Due to these variations and due to the large uncertainties in the reaction scheme, it is not yet possible to obtain a better theoretical representation of the ion abundance in the stratosphere. Furthermore, the relatively good agreement which is obtained at 35 km is somewhat artificial since it is obtained by adjusting some unknown parameters. The interest of such a computation however is to show the coherence of the chemical system which is adopted and in particular to point out that the observed concentrations can be quite well simulated with plausible rate constants. Finally, the model provides concentration values at various heights where no observation is presently available.

#### 4.2. Negative ions

When analyzing the vertical profiles provided by the model for the negative ion concentrations, it appears that the stratosphere can again be divided into two separate regions. Between 35 km and the stratopause, the ion composition is dominated by  $\text{HSO}_4^-$  ion cores which points out the importance of sulfuric acid in the ion budget and consequently the probable relation with the stratospheric aerosols. Below 30 km, most of the ions happen to contain  $\text{NO}_3^-$  cores and are therefore to be controlled by nitric acid. These results are confirmed by the observations of Viggiano and Arnold (1981) (see fig. 6). Both regions of the stratosphere seem thus to be sensitive to anthropogenic activity, in particular to the emission of sulphur and nitrogen compounds respectively.

The calculation of the detailed negative ion composition is not obvious since many rate constants are still unknown. Adopting the values discussed in a previous section with some adjustment (see table



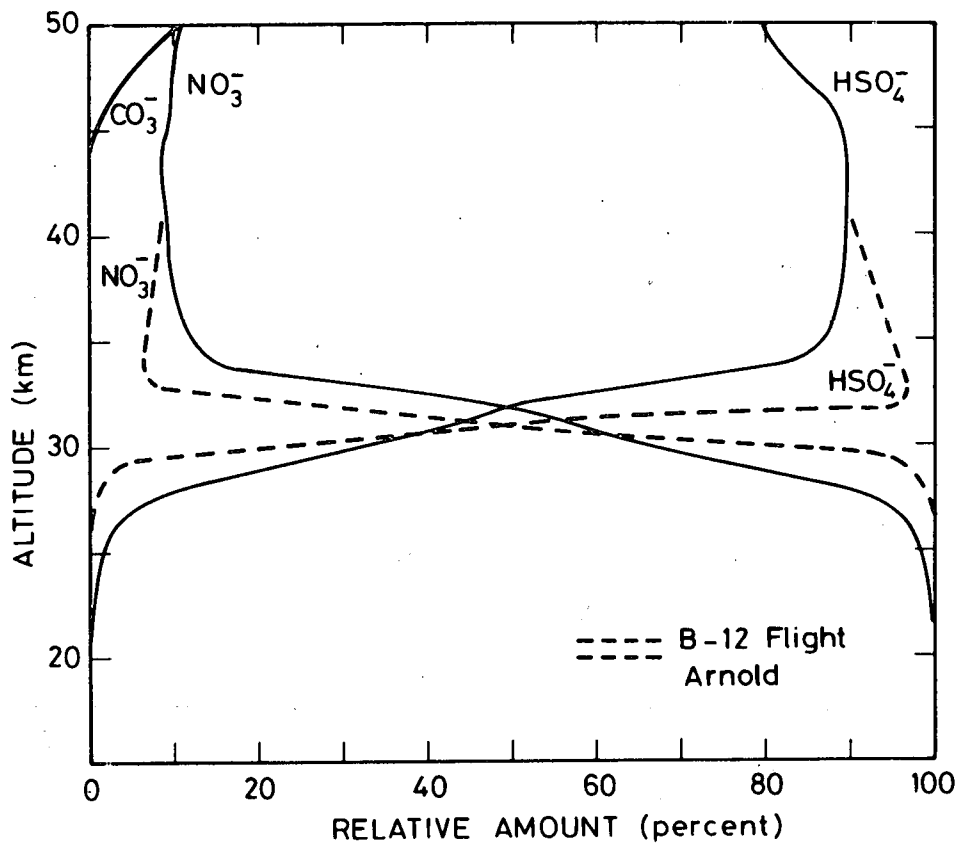


Fig. 6.- Relative amount of the  $\text{HSO}_4^-$  and  $\text{NO}_3^-$  ion cores versus height. Calculated and observed values.

2), the calculated values at 35 km (table 6) are in rather good agreement with the values provided by Arnold et al (1982b) and Arijs et al (1981; 1982b). The model indicates that the most abundant ion should be  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_3$  (mass 391) with a relative amount of about 33 percent. Very recent data obtained by Arnold et al (1982) seem to indicate that the hydration of this latter ion (which was not considered in the model) should be important. If so, the concentration calculated for mass 391 ion should in fact correspond to the total of mass 391 and 409 (and maybe heavier) ions.

The amount at 35 km of several ions, namely  $\text{HSO}_4^- \text{HNO}_3$  (mass 160),  $\text{NO}_3^-(\text{HNO}_3)_2$  (mass 188),  $\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4$  (mass 195) and  $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_2$  (mass 293) is approximatively the same (table 6), which is in good agreement with the observations reported from the september 80 flight by Arijs et al (1981b) and the october 1981 flight by Arnold et al (1982). As indicated by figure 7 however, the composition should change rapidly with altitude. At 30 km for example, the model predicts for  $\text{NO}_3^-(\text{HNO}_3)_2$  a relative ion concentration of 60 percent while 5 km higher this number is reduced to 10 percent only. Above 40 km the  $\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4$  ion (mass 195) becomes, according to the model, the most abundant ion while at 50 km  $\text{HSO}_4^-$  (mass 97) contributes to 20 percent of the ion concentration.

Further comparison with the available observations can be made by calculating the ratio between several ion concentrations. If the family of  $\text{NO}_3^-$  cores are first considered, the  $[\text{NO}_3^-(\text{HNO}_3)_2]/[\text{NO}_3^-(\text{HNO}_3)]$  ratio should be equal to the product of the equilibrium constant  $K_{\text{eq}}$  (61) by the  $\text{HNO}_3$  concentration, if the recombination is much slower than the thermal dissociation of  $\text{NO}_3^-(\text{HNO}_3)_2$ . The model determines at 35 km a ratio of 8.53 which is very close to the value obtained when calculating the  $K_{\text{eq}}$  (61)  $[\text{HNO}_3]$  product (9.63 for  $T = 236.5 \text{ K}$  and  $[\text{HNO}_3] = 2.26 \times 10^{-8} \text{ cm}^{-3}$  or 1.28 ppbv) and to the numbers derived by Arijs et al (1982b) from their sept. 80 and sept. 81 flights (7.7 and 7.1 respectively).

**TABLE 6 :** Comparison of observed and calculated negative ions abundance  
(expressed in percent relative to the total ion density).

<u>Mass</u>	<u>Identification</u>	<u>Observations at ~ 35 km</u>					<u>Model</u>
		Arnold <u>et al.</u> (1981b; 1982)		Arijs <u>et al.</u> (1982b)			35 km
Altitude (km)		36.5	32.9	39.7	35.0	32.5	
Date		Nov. 77	Oct. 81	June 80	Sept. 80	Sept. 80	
Temperature (K)		227	233	239	232	234	237
125	$\text{NO}_3^- \text{HNO}_3$	2.6	6.5	5	2	2	1.2
160	$\text{HSO}_4^- \text{HNO}_3$	5.3	14.0	9	16	10	14.7
188	$\text{NO}_3^- (\text{HNO}_3)_2$	65.6	19.0	8	15	14	13.7
195	$\text{HSO}_4^- \text{H}_2\text{SO}_4$	6.6	10.0	7	14	14	15.9
206	$\text{NO}_3^- (\text{HNO}_3)_2 \text{H}_2\text{O}$	-	-	-	-	3	0.7
223	$\text{HSO}_4^- (\text{HNO}_3)_2$	14.2	1.8	4	5	7	6.8
275	$\text{HSO}_4^- \text{H}_2\text{SO}_4 \text{HNO}_3 \text{H}_2\text{O}$	-	1.0	-	-	3	0.2
293	$\text{HSO}_4^- (\text{H}_2\text{SO}_4)_2$	2.6	12.0	19	14	16	13.6
391	$\text{HSO}_4^- (\text{H}_2\text{SO}_4)_3$	-	14.0	48	34	31	32.8
409	$\text{HSO}_4^- (\text{H}_2\text{SO}_4)_3 \text{H}_2\text{O}$	-	13.0	-	-	-	-

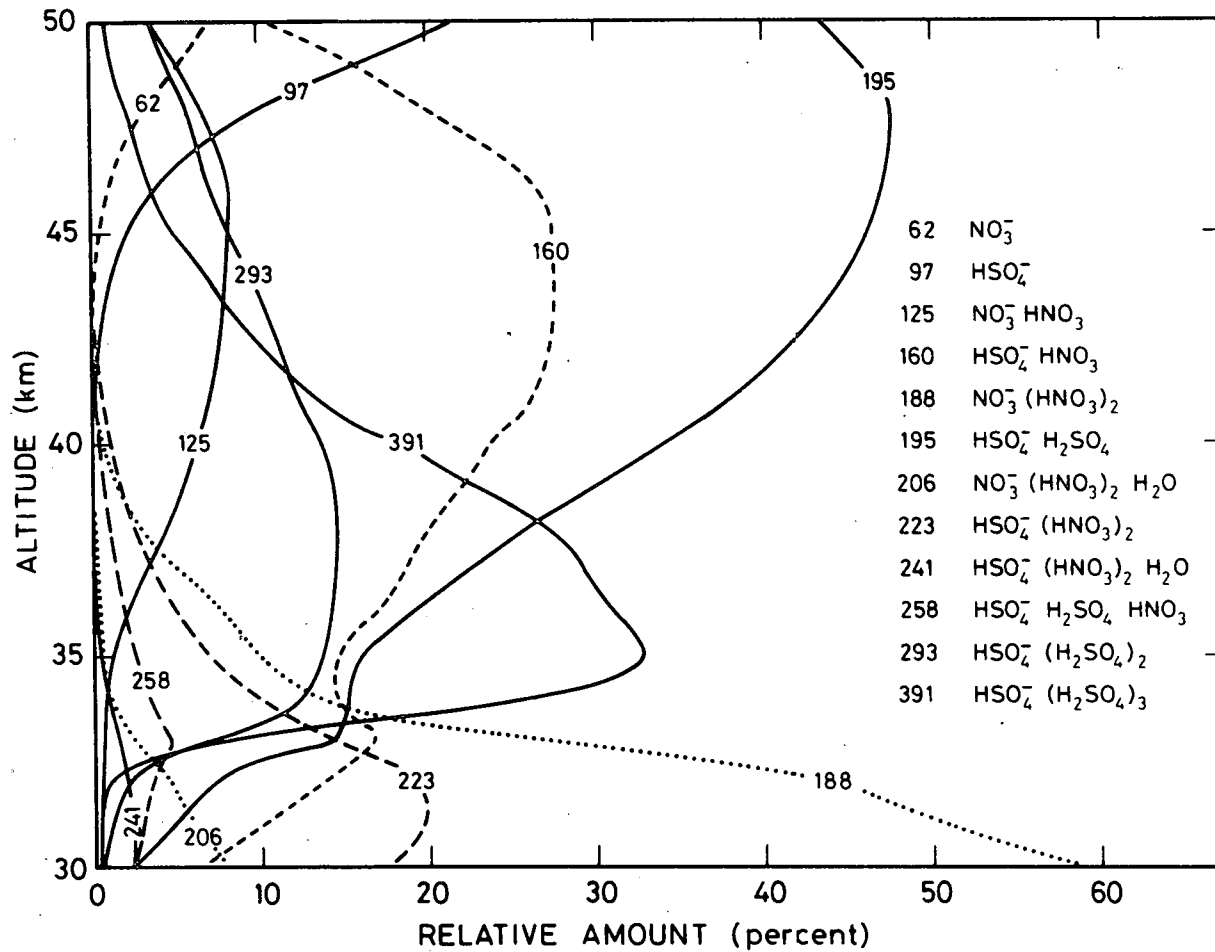


Fig. 7.- Vertical distribution of the relative amount of the most abundant negative ions between 30 and 50 km.

For the sulfate ions, it is convenient, following Arnold *et al* (1981b) to consider various subfamilies based on the numbers of  $\text{H}_2\text{SO}_4$  molecules present in the cluster. Using the family nomenclature suggested by Arijs *et al* (1982b), we define  $F_m$  as the ions of the form  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_m (\text{HNO}_3)_i$  and  $F_{-1}$  the  $\text{NO}_3^-(\text{HNO}_3)_i$  ions. As in the case of the positive ions, we calculate the ratios

$$R_\ell = \sum_{i=\ell}^{i_{\max}} [F_i]/[F_{\ell-1}] \quad (14)$$

In practice, the summation is done only up to  $i_{\max} = 3$ . These ratios express the magnitude of the conversion from the  $F_{\ell-1}$  to the  $F_\ell$  subfamily. When the main loss process for these ions is recombination,

$$R_\ell = k_\ell [\text{H}_2\text{SO}_4]/\alpha[n^+] \quad (15)$$

where  $k_\ell$  is an effective rate constant for the  $F_{\ell-1}$  to  $F_\ell$  conversion. Adopting the values used in the model at 35 km, namely  $[\text{H}_2\text{SO}_4] = 2.16 \text{ cm}^{-3}$ ,  $\alpha = 7.67 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ ,  $[n^+] = 3.63 \times 10^3 \text{ cm}^{-3}$ , the ratio  $R_\ell$  is equal to 7.75 for a conversion rate  $k_\ell$  of  $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . Since rate constants  $k_{60}$  and  $k_{64}$  measured by Viggiano *et al* (1982) are a factor of 2 to 5 larger than the values imposed in the model for  $k_{67}$  and  $k_{70}$  ( $5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ), one should expect at least a factor of 2 difference in the calculated values of  $R_0$  and  $R_1$ . This is the case as shown by table 7. The determination of  $R_2$  and  $R_3$  needs to take into account the clustering mechanisms and the thermal decomposition of  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_\ell$ . For example, the  $R_3$  ratio is given by

$$R_3 = \frac{k_f(81) [M] [\text{H}_2\text{SO}_4]}{k_r(81) [M] + \alpha[n^+]} \cong K_{\text{eq}}(81) [\text{H}_2\text{SO}_4] \quad (16)$$

and is of the order of 2.5 at 35 km when the model conditions are adopted. Table 7 indicated that the calculated  $R_{\ell}$  ratios are coherent and are in rather good agreement with the corresponding values derived from the observed abundances.

Again, it should be remembered that these results are obtained by adjusting some parameters at the observation level of 35 km. The fact that no temperature dependence has been introduced when specifying the equilibrium constants of several important reactions, could seriously modify the overall picture given by fig. 7 and even alter the overall conclusions.

In the absence of new laboratory data for the ion kinetics, in situ observations of the composition at different heights (and at different temperature) should permit to derive a crude temperature dependence of the most important constants.

## 5. SUMMARY AND CONCLUSIONS

A model of the ion composition in the stratosphere has been developed in order to study the major chemical processes related to positive and negative ions. In order to validate such a model, theoretical results should be obtained independently from any observational data. However, since the chemical kinetics is still poorly known, some input parameters have yet to be based on in situ measurements. The comparison between observed and calculated concentration should therefore be made with care. It remains also difficult because of the break-up in the instrument of the heavier ions leading to an under-estimation of their atmospheric concentration and consequently an over-estimation of the light ions amount. At the present time, stratospheric ion models show the consistency of the chemical scheme derived from in situ measurements and should be improved in the future.

**TABLE 7 :** Abundances at 35 km of subfamilies  $F_\ell$  (expressed in percent) and  $R_\ell$  ratios. Comparison between in situ measurements obtained from different flights and calculated values.

	Observations (~ 35 km)					Model (35km)
	Arnold <u>et al</u> (1981b; 1982)		Arijs <u>et al</u> (1982b)			
	Nov. 77	Oct. 81	June 80	Sept. 80	Sept. 81	
$F_{-1} = \text{NO}_3^-(\text{HNO}_3)_\ell$	68.2	25.5	13	17	16	11.2
$F_0 = \text{HSO}_4^-(\text{HNO}_3)_i$	19.5	15.8	13	21	17	21.5
$F_1 = \text{HSO}_4^-(\text{H}_2\text{SO}_4)(\text{HNO}_3)_j$	9.7	11.0	7	14	17	20.9
$F_2 = \text{HSO}_4^-(\text{H}_2\text{SO}_4)_2(\text{HNO}_3)$	2.6	12.0	19	14	16	14.1
$F_3 = \text{HSO}_4^-(\text{H}_2\text{SO}_4)_3(\text{HNO}_3)_\ell$	-	27.0	48	34	31	31.1
$R_0 = (F_0 + F_1 + F_2 + F_3)/F_{-1}$	0.47	2.60	6.69	4.88	4.75	7.83
$R_1 = (F_1 + F_2 + F_3)/F_0$	0.63	3.16	5.69	2.95	5.33	3.07
$R_2 = (F_2 + F_3)/F_1$	0.27	3.54	9.57	3.43	2.76	2.16
$R_3 = F_3/F_2$	0	2.25	2.52	2.43	1.94	2.21

The chemical kinetics related to the positive ions is somewhat better known than in the case of the negative ions. Further progress however requires a better understanding of the atmospheric budget of acetonitrile and methanol and a better knowledge of the rate and equilibrium constants versus temperature for reactions as given by equations (6) and (7).

The composition of the negative ions in the stratosphere seems driven by nitric and sulfuric acid. The calculated mixing ratio of  $\text{HNO}_3$  is a factor of 2 larger than the observed values and some work is thus required to understand this discrepancy. The atmospheric budget of sulfur is not completely understood and it is therefore difficult to derive a precise concentration value of  $\text{H}_2\text{SO}_4$  in the upper stratosphere. The reaction rates and the equilibrium constants for most chemical processes involved in the stratospheric negative ion budget have never been measured except for a few reactions. Laboratory work is thus required and should permit to simplify the adopted chemical value by neglecting the minor reaction paths. New spectrometric observations should consider the possible existence of heavier ions or ion complexes involving solid or liquid particles. Further theoretical work should take into account the possibility of heterogenous processes and a strong coupling between ions and aerosol.

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