Theoretical Notes
Note 340

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AIR CHEMISTRY RELATING TO EMP

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The calculation of the ion and electron densities for systems purposes is usually accomplished by use of a simple model involving only one positive ion species, n_+, and one negative ion species, n_-, in addition to the electron density, n_e,

$$\frac{dn_e}{dt} = q - \alpha_d n_+ n_e - An_e + Dn_- \qquad (1)$$

$$\frac{dn_+}{} = q - \alpha_d n_+ n_e - \alpha_i n_- n_+ \quad , \qquad (2)$$

$$\frac{dn_-}{dt} = An_e - Dn_- - \alpha_i n_- n_+ \quad , \qquad (3)$$

where q is the ion pair production rate, α_d is the electron-ion recombination coefficient, α_i is the ion-ion recombination coefficient, D is the electron detachment coefficient, and A is the electron attachment coefficient. The equations are not independent and one can be eliminated by use of the charge conservation condition,

$$n_+ = n_- + n_e \quad . \qquad (4)$$

The above equations constitute an enormous simplification. The actual deionization process in air can involve 50 or more different ion species and almost as many neutral species. This complexity is gathered into the coefficients α_d, α_i, D and A. These are, in general, functions of altitude, temperature, ambient air composition and ionization rate, q.

In Table 1 we have listed most of the positive ions which, under various conditions, are important in the deionization processess in air.

Table 1 - Air Positive Ions

N^+	NO^+	NO_2^+
N_2^+	$NO^+ \cdot NO$	$NO_2^+ \cdot (H_2O)_{n=1,2}$
O^+	$NO^+ \cdot (H_2O)_{n=1,2,3}$	$NO_2^+ \cdot N_2$
O_2^+	$NO^+ \cdot N_2$	$NO_2^+ \cdot CO_2$
$N^+ \cdot N_2$	$NO^+ \cdot CO_2$	$NO_2^+ \cdot N_2 \cdot H_2O$
$N_2^+ \cdot N_2$	$NO^+ \cdot N_2 \cdot (H_2O)_{n=1,2}$	$NO_2^+ \cdot CO_2 \cdot H_2O$
$O_2^+ \cdot O_2$	$NO^+ \cdot CO_2 \cdot (H_2O)_{n=1,2}$	$H_3O^+ \cdot OH$
$O_2^+ \cdot H_2O$		$H_3O^+ \cdot (H_2O)_{n=0,1,...?}$
H_2O^+		

The first four of the ions in the first column can be considered to be the initial ions formed upon the deposition of radiative energy. These ions then undergo a series of charge transfer, ion-atom iterchange, and clustering reactions. If recombination with electrons or negative ions does not occur along the way, these processes result in the formation of the last ion in the third column. These ions, with n up to four, have been observed as being the dominant ions as high as 70 or more kilometers altitude. Ions with n much higher have been observed in the laboratory and at sea level they are expected to be present. The time for these ions to form and become dominant depends on the air and water vapor densities and ranges from much less than a microsecond at sea level to hours at 70 kilometers. There are several paths which can be taken to form these hydrated hydronium ions, depending on whether O_2^+, NO^+ or NO_2^+ is the dominant ion formed early in the process. The paths involving NO^+ or NO_2^+ are not well understood. Fortunately, at least for our purposes, in highly disturbed air the primary ion formed initially or very soon after is O_2^+ and this path is fairly well understood. A schematic of this is shown in Figure 1.

It is obvious that the formation of each $H_3O^+ \cdot (H_2O)_n$ from the initial air ions results in the production of a hydroxl radical, OH. When a $H_3O^+ \cdot (H_2O)_n$ recombines with an electron or negative ion another species containing a single H atom is produced. The products of such ion-ion recombinations are not known and we have assumed a free H is produced. The hydration process and eventual recombination is the most important source of "odd hydrogen".

Fortunately, the electron recombination coefficient, which increases with cluster size, does not vary significantly above n equal to two or three. At high values of n the electron recombination rate coefficient levels off and is equal to a value of about 7×10^{-6} cm^3/sec. Since the α_d for the initial diatomic ions is about 2×10^{-7} cm^3/sec, α_d will vary considerably until the quasi-steady positive ion distribution is attained. Since the final ion distribution depends on temperature, density, water vapor density and electron and negative ion concentrations, the α_d will thus be a function not only of time but also of altitude and ion-pair production rate, q. At sea level the large air and water vapor densities dominate and, as mentioned before, the large cluster ions form very quickly. If, however, the energy deposition is large enough to significantly heat the air, the large clusters tend to break up. An example of this is shown in Figures 2 and 3. Figure 2 shows a ion-pair production rate time history for a point near a high yield sea level burst. The air temperatures are also shown. Figure 3 shows the values of α_d as a function of time. We can see the rapid increase in α_d due to clustering at early times and the drop at later times due the temperature rise.

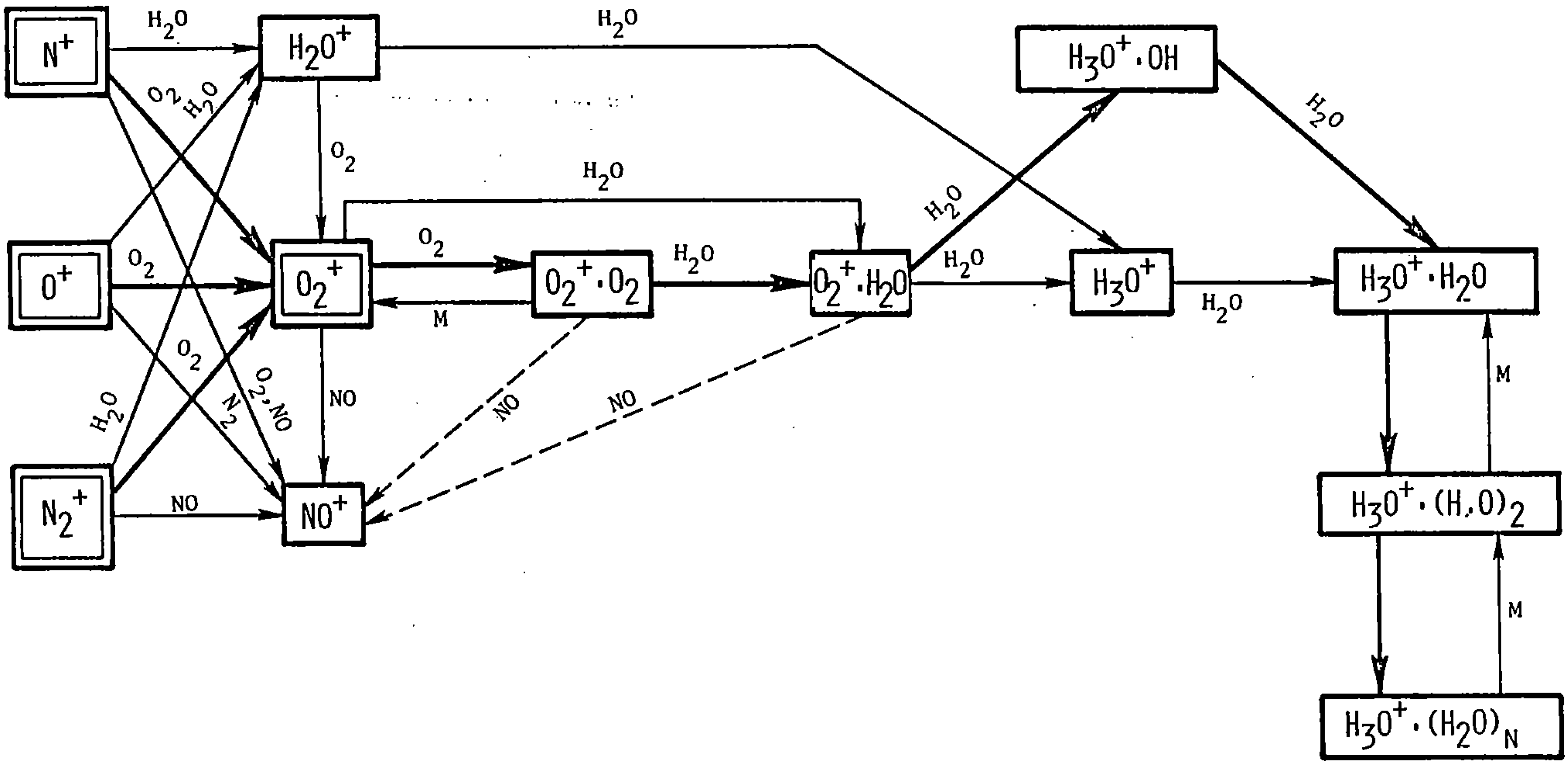
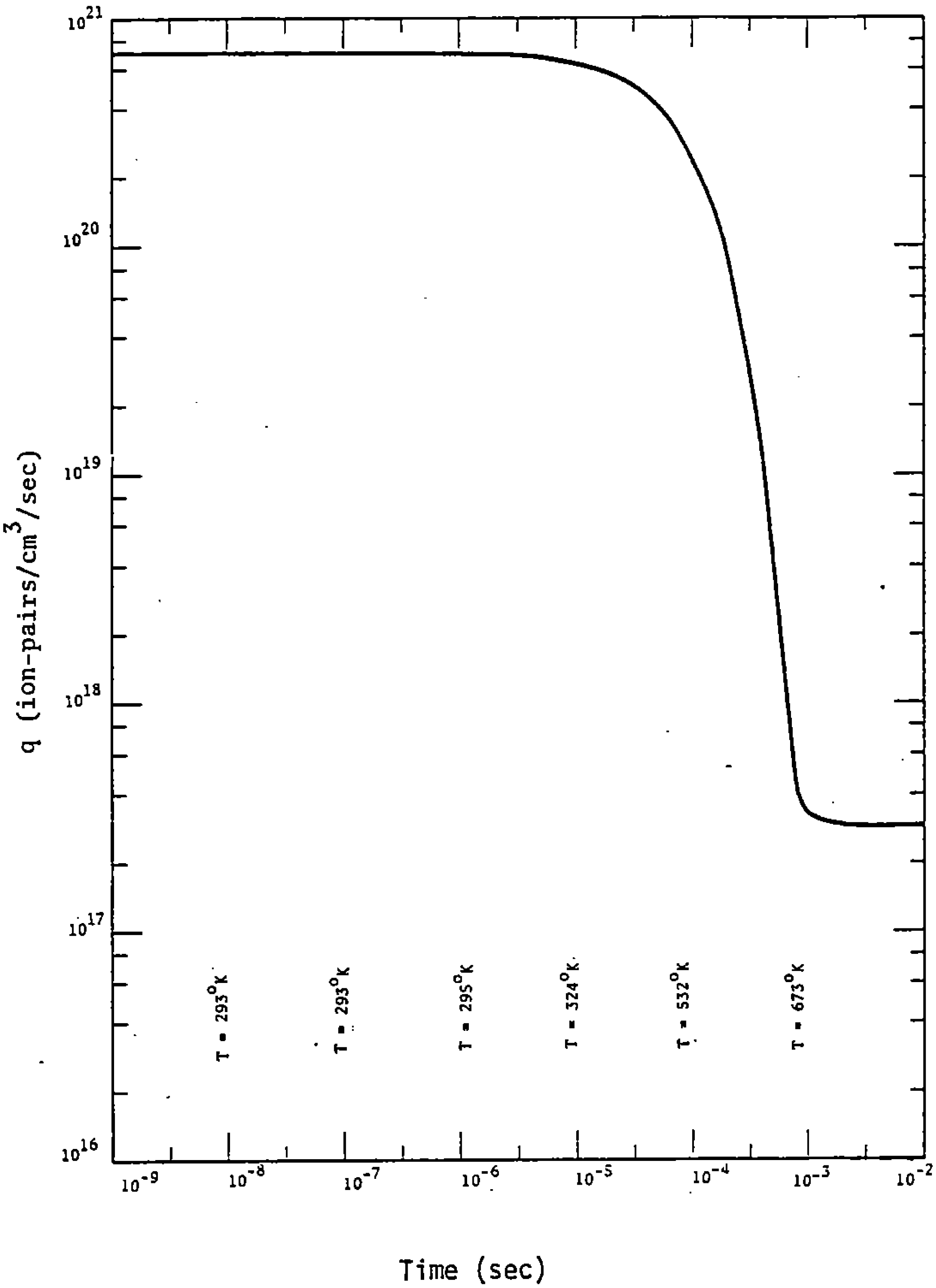

N+
O+
N2+
H2O+
O2+
NO+
O2+·O2
O2+·H2O
H3O+
H3O+·OH
H3O+·H2O
H3O+·(H,O)2
H3O+·(H2O)N
H2O
O2
NO
N2
O2,NO
M

Figure 1.



q (ion-pairs/cm3/sec)
10^21
10^20
10^19
10^18
10^17
10^16
T = 293°K
T = 293°K
T = 295°K
T = 324°K
T = 532°K
T = 673°K
10^-9
10^-8
10^-7
10^-6
10^-5
10^-4
10^-3
10^-2
Time (sec)

Figure 2.

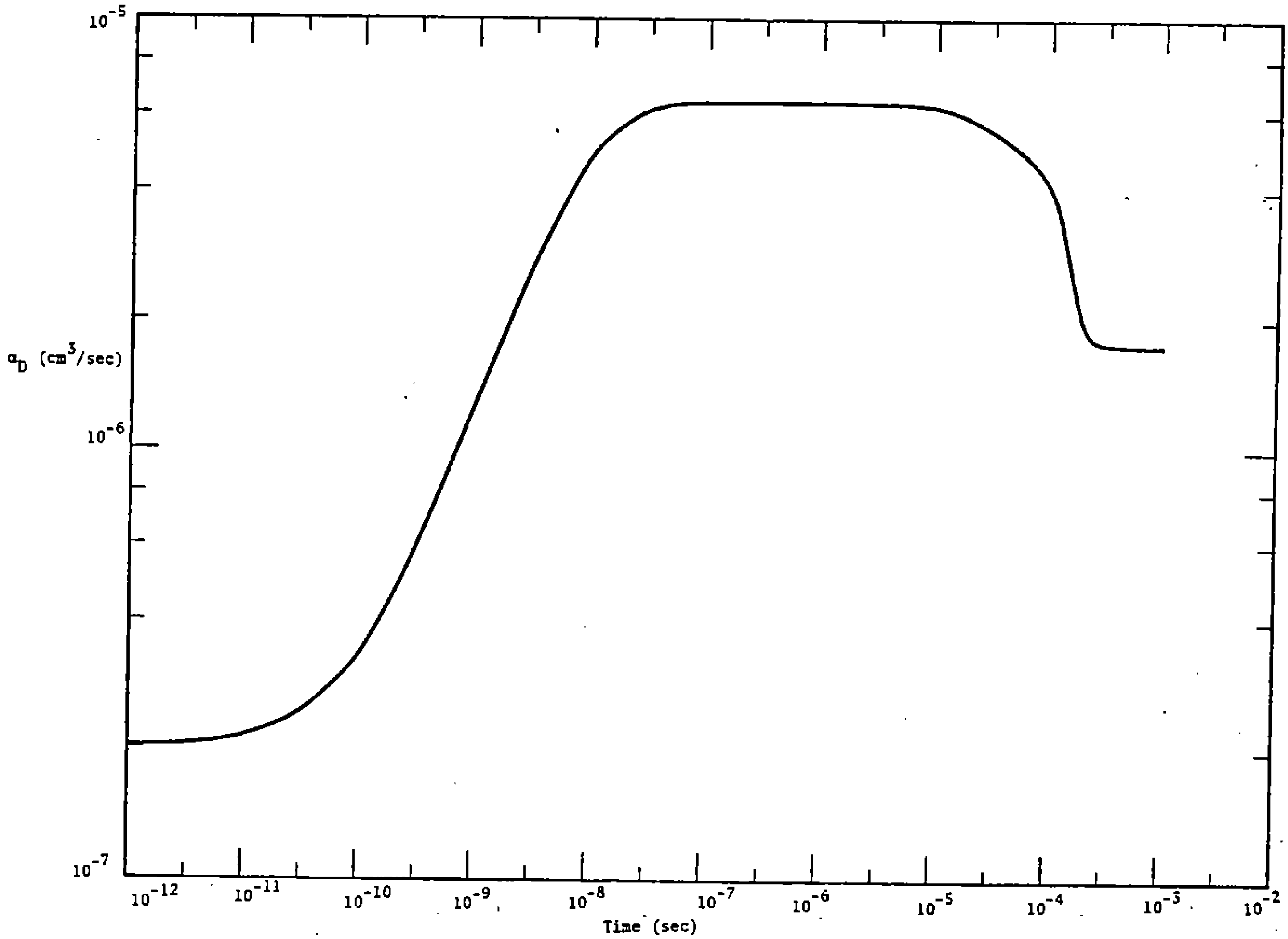

10^{-5}
α_D (cm^3/sec)
10^{-6}
10^{-7}
10^{-12} 10^{-11} 10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2}
Time (sec)

Figure 3.

In Table 2 we have listed some of the primary negative ions of importance.

Table 2 - Air Negative Ions

O^-	NO_2^-	CO_3^-
O_2^-	NO_3^-	CO_4^-
O_3^-	$NO \cdot O_2^-$	OH^-
O_4^-	Clusters	

The species designated $NO \cdot O_2^-$ has a different, less stable, structure than NO_3^- and is formed by and enters into different reactions. All or most of the negative ions shown cluster with water and other molecules. Clusters involving HNO_3 seems to be particularly stable. The negative ion clusters are formed more slowly than the positive ion clusters and are not as important to the deionization chemistry since the two body ion-ion recombination rate coefficients do not seem to be strongly dependent on whether the ions are clustered or not. This, however, is uncertain and a point of some controversy. Direct measurements of ion-ion recombination coefficients are difficult and very few have been made. One set of measurements using simple unclustered ions have yielded values between 10^{-7} and $5x10^{-7}$ cm^3/sec. A more recent set of measurements, using a different technique and using both clustered and unclustered ions has yielded a value of about $6x10^{-8}$ cm^3/sec regardless of the ions involved. This value is in better agreement with values derived indirectly from field test data. Also the ions in the first set of experiments may have been in excited states. For these reasons the value of $6x10^{-8}$ cm^3/sec has been adopted for all ions. The question, however, is by no means settled.

At low altitudes three-body ion-ion recombination is probably dominant but no direct data at all is available for clustered ions. A rate coefficient of about 10^{-25} cm^3/sec is generally used and at sea level this is about forty times the two-body rate coefficient. The three body process will dominate, therefore, up to about 40 kilometers altitude.

The detachment coefficient arises from the fact all the negative ions are subject to ionization processes. Some negative ions, such as O^-, O_2^- and OH^-, are very easily ionized by chemical reaction. Examples of these reactions and their rate constants are:

$$
\begin{aligned}
&O^- + O \rightarrow O_2 + e, && k = 2\times10^{-10}\ \mathrm{cm^3/sec}\\
&O^- + N \rightarrow NO + e, && k = 2\times10^{-10}\ \mathrm{cm^3/sec}\\
&O^- + NO \rightarrow NO_2 + e, && k = 2.5\times10^{-10}\ \mathrm{cm^3/sec}\\
&O_2^- + O \rightarrow O_3 + e, && k = 1.5\times10^{-10}\ \mathrm{cm^3/sec}\\
&O_2^- + N \rightarrow NO_2 + e, && k = 3\times10^{-10}\ \mathrm{cm^3/sec}\\
&O_2^- + O_2(^1\Delta) \rightarrow O_2 + O_2 + e, && k = 2\times10^{-10}\ \mathrm{cm^3/sec}\\
&OH^- + H \rightarrow H_2O + e, && k = 1.4\times10^{-9}\ \mathrm{cm^3/sec}
\end{aligned}
\qquad (5)
$$

Ions such as NO_2^- and NO_3^- are not detachable by chemical means and are usually destroyed only by recombination with positive ions.

Ions such as O_3^- and CO_3^- are intermediate ions. Though not directly detachable by chemical reaction they can be converted to detachable ions by reactions such as:

$$
\begin{aligned}
&O_3^- + O \rightarrow O_2^- + O_2, && k = 2.5\times10^{-10}\ \mathrm{cm^3/sec}\\
&CO_3^- + O \rightarrow O_2^- + CO_2, && k = 1.1\times10^{-10}\ \mathrm{cm^3/sec}\\
&CO_3^- + H \rightarrow OH^- + CO_2, && k = 1.7\times10^{-10}\ \mathrm{cm^3/sec}\\
&O_3^- + H \rightarrow OH^- + O_2, && k = 8.4\times10^{-10}\ \mathrm{cm^3/sec}
\end{aligned}
\qquad (6)
$$

or they can be converted to NO_2^- and NO_3^- by reactions with NO, NO_2, HNO_2, and HNO_3.

All negative ions are subject to photodetachment by either sunlight or fireball light. NO_2^- and NO_3^- are much less susceptible to photodetechment than are O^- and O_2^- because of their larger ionization potentials.

It is obvious that the detachment coefficient, like the electron-ion recombination coefficient, will be a complicated function of time, altitude, neutral atom and molecule composition, and q.

Detachment processes can be very important in the upper D-region but at low altitudes one has to get very close to a fireball at very early times for it to be important. This is fortunate, since the negative ions at low altitudes will almost certainly be hydrated and we know very little concerning the detachment of such ions.

Generally, the attachment coefficient, A, is the simplest of the coefficients. It can usually be associated with the three body attachment of electrons to the oxygen molecule, i.e.,

$$e + O_2 + M \rightarrow O_2^- + M \quad . \qquad (7)$$

where M is O_2, N_2 or H_2O. The attachment coefficient is then

$$A = \sum_j k_j (O_2)(M_j) \quad . \qquad (8)$$

where k_j is the rate coefficient of the attachment reaction with M_j as the third body. The parentheses indicate concentrations.

The value of the attachment coefficient from Reaction 7 is of the order of 10^8 sec^{-1} at sea level. Other species will attach electrons. For instance we have

Table 3

Species	Production Per Ion-Pair
O	0.20
N	0.46
$O(^1D)$	0.10
$N(^2D)$	0.60
$N_2(A)$	0.50
$O_2(^1\Delta)$	0.60
$O_2(^1\Sigma)$	0.10

These species are formed during the rapid thermalization of the high energy electrons produced by the initial energy deposition. Because of the uncertainties in the cross sections involved in this calculation some of the values have considerable uncertainty. The largest uncertainties are in the values for N, $N(^2D)$ and $O_2(^1\Delta)$. There is also some indication that the values for neutron deposition are different from those for gama, beta and X-ray deposition.

The excited states of molecular oxygen do not have a significant role in the formation of HNO_3 and we need not say any more about them. The $N_2(A)$ that is formed reacts rapidly with molecular oxygen. The predominant channel is assumed to be that which dissociates the oxygen, i.e.,

$$N_2(A) + O_2 \rightarrow N_2 + O + O \qquad (12)$$

The reaction of $N_2(A)$ with H_2O is unknown and this is another of the many uncertainties we will encounter.

$$e + O_3 \rightarrow O_2 + O^- \quad , \quad k = 9x10^{-12}\ cm^3/sec \qquad (9)$$

$$e + NO_2 \rightarrow NO_2^- \quad , \quad k = 4x10^{-11}\ cm^3/sec \qquad (10)$$

A nculear burst will produce O_3 and NO_2 and at high altitudes Reactions 9 and 10 may contribute significantly to the attachment coefficient. At sea level, however, they do not.

Recently the rate constant for the reaction

$$e + HNO_3 \rightarrow NO_2^- + OH \qquad (11)$$

was measured to be $5x10^{-8}\ cm^3/sec$, an unusally high value. Thus, an HNO_3 concentration of about $2x10^{15}\ cm^{-3}$ or more would make Reaction 11 competitive with Reaction 7. The ambient concentrations of HNO_3 are certainly nowhere near this value, but the chemistry following the deposition of a large amount of energy could result in the formation of sufficient HNO_3 to make Reaction 11 important. This chemistry is rather complicated, and begins with the species formed by the initial deposition of energy.

In addition to ions such as N_2^+ , O_2^+ , N^+ and O^+ , the deposition of energy from a nuclear source (neutrons, X-rays, betas and gammas) forms a number of neutral species not usually found in the low altitude atmosphere. The following table lists these species together with the best knowledge of the amount generated per ion-pair produced. When no electronic state is indicated the ground state is assumed.

The $O(^1D)$ is primarily quenched by N_2 but at sea level a significant fraction (20 to 50%) reacts with H_2O to yield two hydroxyl radicals, i.e.,

$$O(^1D) + H_2O \rightarrow OH + OH \quad . \tag{13}$$

The $N(^2D)$ ordinarily reacts very rapidly with molecular oxygen to form nitric oxide,

$$N(^2D) + O_2 \rightarrow N + NO \quad . \tag{14}$$

However, at sea level, there is enough water vapor so that the main quenching of $N(^2D)$ is accomplished by H_2O. The rate is fast but the products are unknown. The most likely case is

$$N(^2D) + H_2O \rightarrow NH + OH \tag{15}$$

Figures 4 and 5 show schematically the reaction schemes in which "odd nitrogen" and "odd hydrogen" are involved. The double lines around some of the boxes indicate the species which are formed initially or very early and are the starting points in chemical schemes. Dotted lines between the boxes indicate assumed reaction paths. The heavy lines indicate the major reaction paths.

To obtain an idea of what effect the formation of HNO_3 might have on the attachment coefficient we have calculated the chemistry for the ion source shown in Figure 1. The calculation was for sea level with 4% water vapor concentration. We used our DCHEM code which integrates the coupled chemical rate equations. The code contains 64 species and therefore 64 rate equations. Aside from the ion-ion recombination reactions the code contains 422 reactions. The ion-ion reactions comprise another 580 reactions. This would make over 1000 reactions. However,

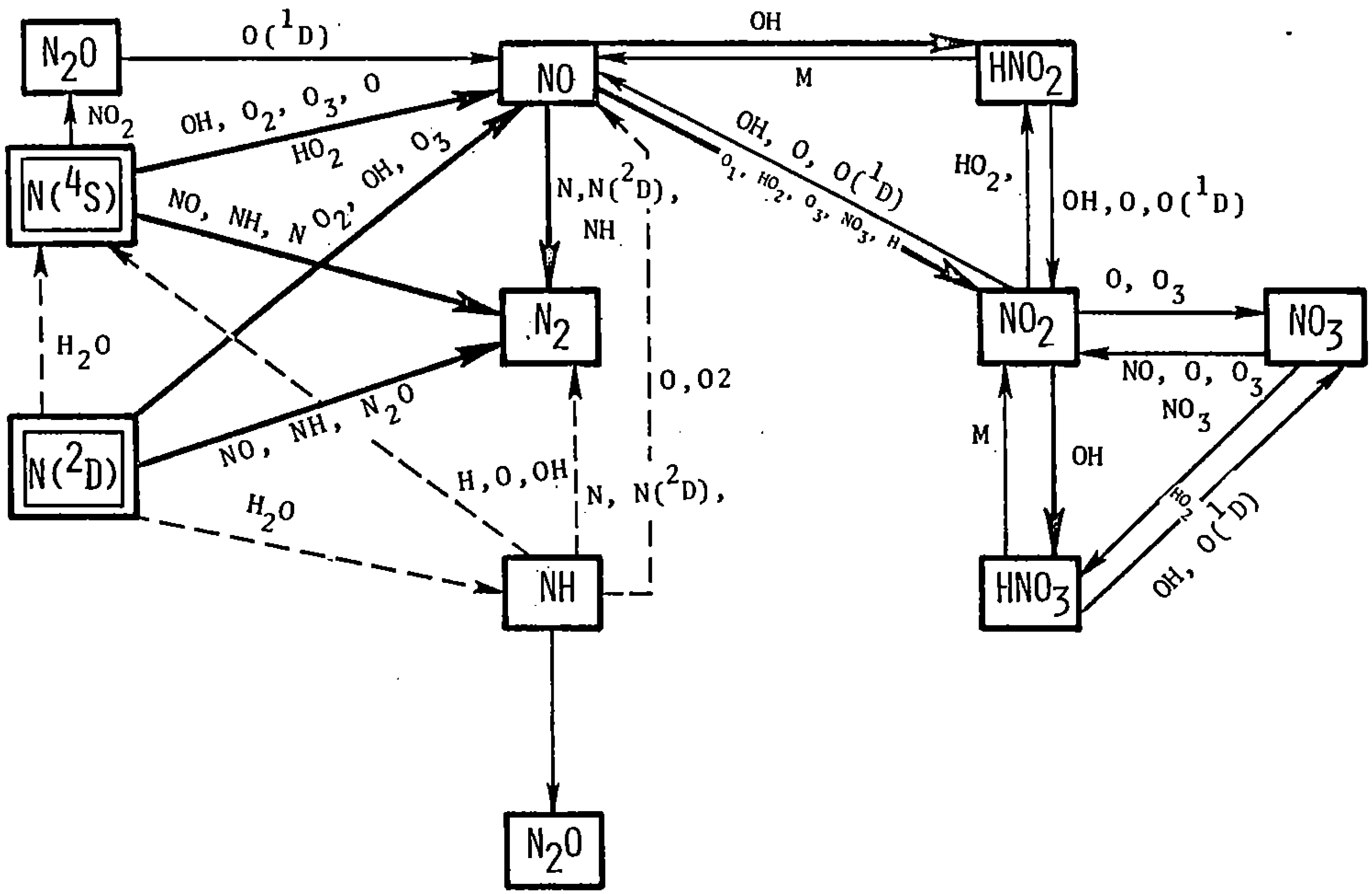

N2O
O(1D)
NO
OH
M
HNO2
NO2
OH, O2, O3, O
HO2
N(4S)
NO, NH, N O2, OH, O3
N,N(2D),
NH
OH, O, O(1D)
O1, HO2, O3, NO3, H
HO2,
OH,O,O(1D)
N2
H2O
N(2D)
NO, NH, N2O
O,O2
O, O3
NO3
NO, O, O3
NO3
M
OH
H,O,OH
N, N(2D),
H2O
NH
HNO3
HO2
OH, O(1D)
N2O

Figure 4.

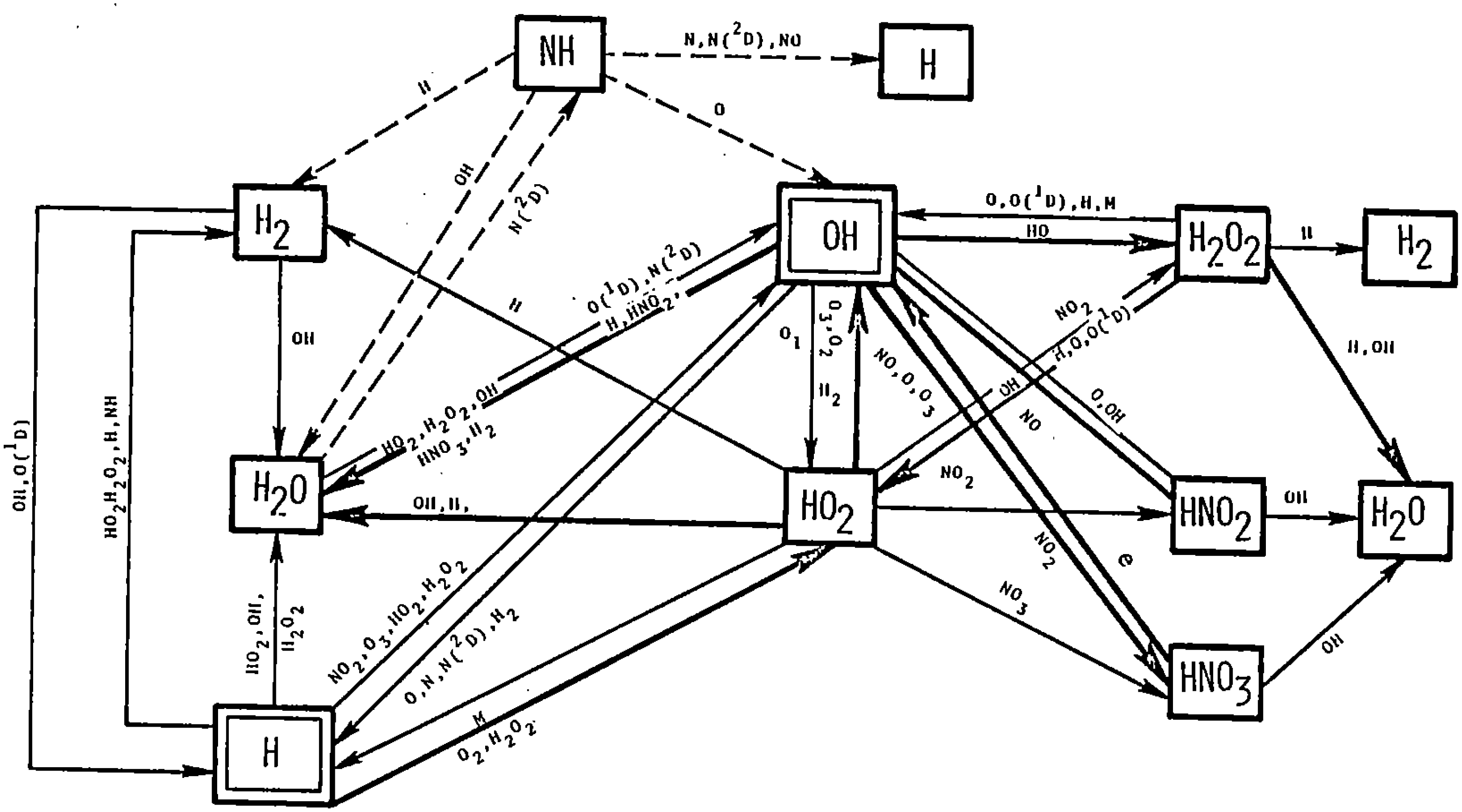


Figure 5.

since the ion-ion rates we have used are independent of the identity of the ions we can lump the 580 reactions into 78 equivalent reactions. Thus we have 500 reactions.

Figures 6 and 7 show a number of species as a function of time. The HNO_3 is formed primarily by the reaction.

$$NO_2 + OH \rightarrow HNO_3 \quad , k = 1.1x10^{-11} \text{ cm}^3/\text{sec} \qquad (16)$$

This is really a three-body reaction but at sea level it is saturated and is expressed as a two-body reaction. The NO is oxidized primarily by the reaction

$$NO + HO_2 \rightarrow NO_2 + OH \quad ; k = 8.1x10^{-12} \text{ cm}^3/\text{sec} \qquad (17)$$

During these processes the OH and HO_2 are being rapidly depleted by the reaction

$$OH + HO_2 \rightarrow H_2O + O_2 \quad , k = 2x10^{-11} \text{ cm}^3/\text{sec} \qquad (18)$$

Thus when the "odd hydrogen" disappears back into H_2O, the NO, NO_2 and HNO_3 concentrations stabalize. A similar situation applies to HNO_2.

The attachment rate at 10^{-3} seconds is $5.7x10^{8}$ sec^{-1} or about four times the rate when only attachment to O_2 is considered.

We see that any process which decreases the oxidation of NO (Equation 17) or which dissociates NO_2 will decrease the HNO_3 concentration and thus the attachment rate. Such a process is photodissociation of NO_2 and HO_2 by bomblight. This has not yet been included in our calculations.

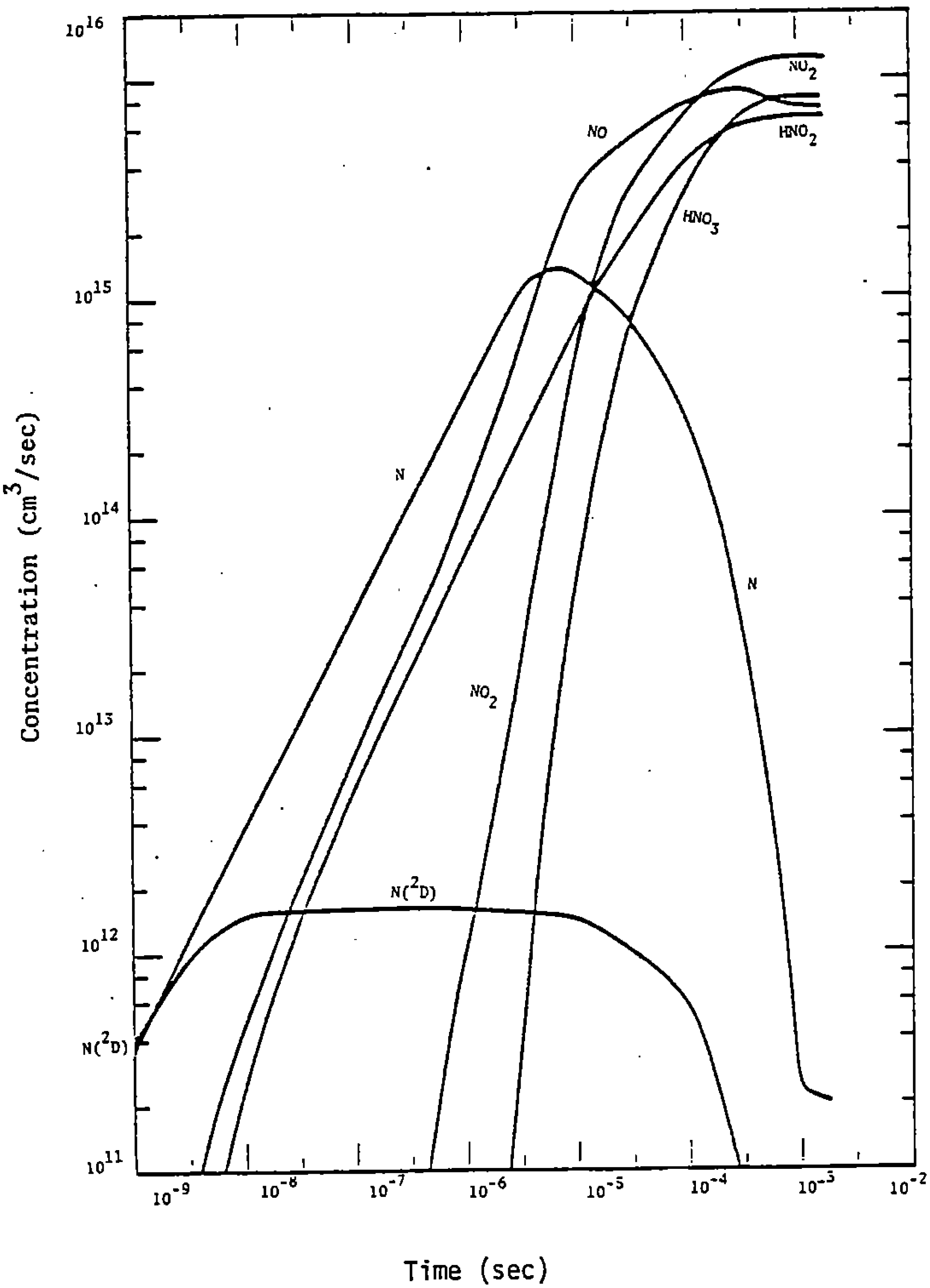
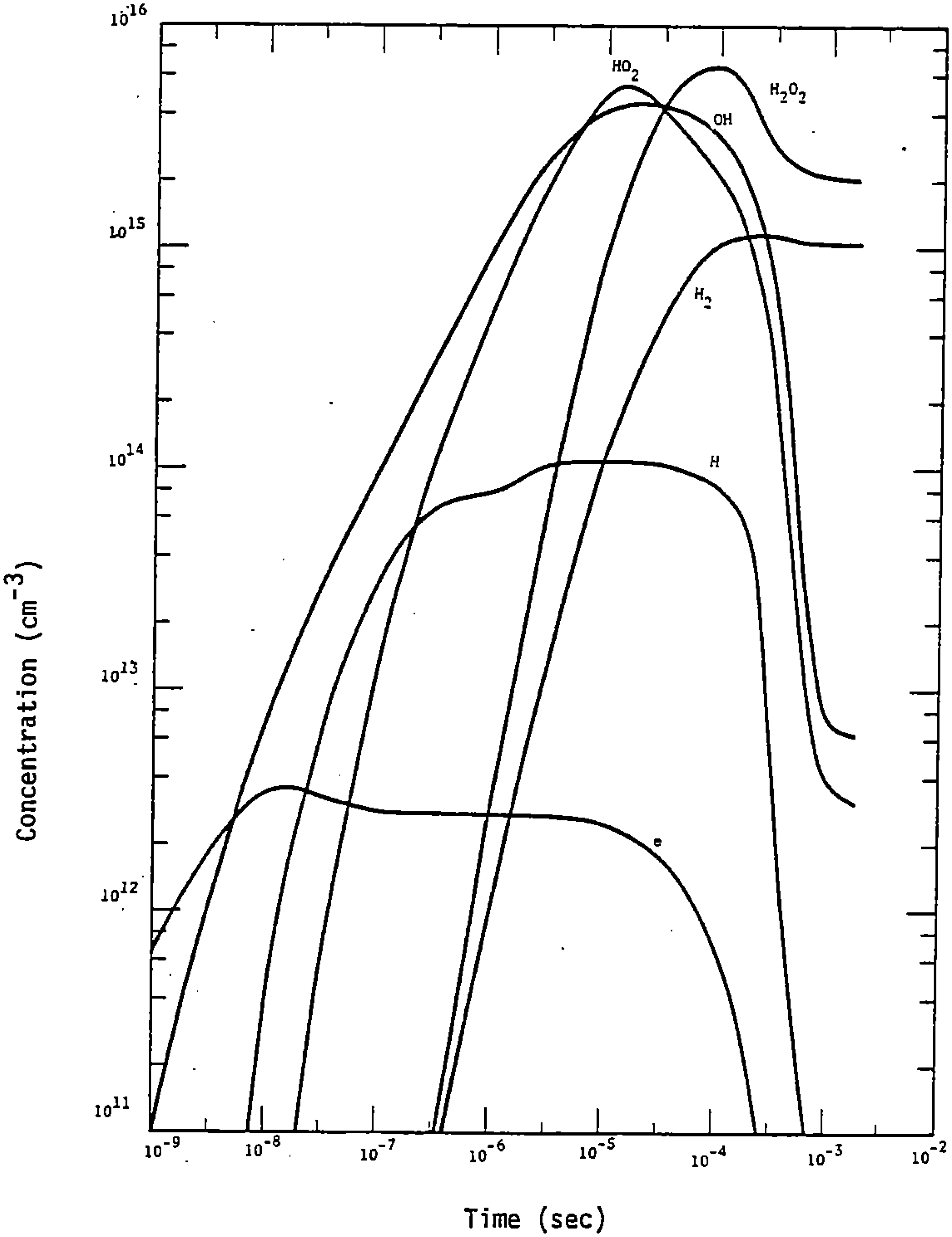

Concentration (cm3/sec)
Time (sec)
NO2
NO
HNO2
HNO3
N
NO2
N
N(2D)
N(2D)

Figure 6.



10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
Concentration (cm^{-3})
HO_2
H_2O_2
OH
H_2
H
e
10^{-9}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
Time (sec)

Figure 7.

We have already mentioned a number of uncertainties involved in this calculation. There is the lack of knowledge as the products of the reactions of $N(^2D)$ and $N_2(A)$ with water vapor and $H_3O^+ \cdot (H_2O)_n$ with negative ions. We also have very little knowledge as to the temperature dependence of most of the important reactions between 200°K and 1000°K. There may also be species and reactions involved which we have not yet considered.

The most important uncertainty, however, is in the photodissociation of HO_2, NO_2 and perhaps HNO_3 by bomblight. At times prior to 10^{-3} seconds the fireball certainly radiates enough energy at the right frequencies to dissociate these species but much of this light is absorbed before it reaches the point in question. What the radiant flux is, as a function of frequency, time and distance, is extremely difficult to calculate. There is evidence that the amount of NO_2 we have calculated is too large and thus the HNO_3 would also be too large. An estimate of the photodissociation (and also photodetachment) should and will be made.

Finally we should mention an effect we have not yet included in our calculations. At the distances and times under consideration the electric fields are such that the electrons can have considerably higher kinetic energies than those of the atomic and molecular species. Energies of up to an electron volt are not uncommon. These electrons can enter into endothermic dissociative attachment reactions which are generally unimportant but which may now be significant because of the high electron energy. Examples of such reactions, together with the energies required to make them go are listed below:

$$e + O_3 \rightarrow O_2^- + O - 0.62 \text{ eV} \quad (18)$$

$$e + HO_2 \rightarrow OH^- + O - 0.89 \text{ eV} \quad (19)$$

$$e + NO_2 \rightarrow O^- + NO - 1.65 \text{ eV} \quad (20)$$

$$e + H_2O \rightarrow OH^- + H - 3.29 \text{ eV} \quad (21)$$

$$e + H_2O_2 \rightarrow OH^- + OH - 0.33 \text{ eV} \quad (22)$$

$$e + HNO_2 \rightarrow OH^- + NO - 0.26 \text{ eV} \quad (23)$$

The rate coefficients of the reverse reactions of 16, 17, 18 and 19 are known to be very large so we would expect these reactions to go very fast if the required kinetic energies are available. Inclusion of these reactions could possibly increase the attachment coefficient significantly and this will be investigated in the near future.