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Chemical Kinetics of Flue Gas Cleaning by Electron Beam

H. Mätzing
Laboratorium für Aerosolphysik und Filtertechnik

Kernforschungszentrum Karlsruhe

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H. Mätzing

Kernforschungszentrum Karlsruhe GmbH, Karlsruhe

Kernforschungszentrum Karlsruhe GmbH
Postfach 3640, 7500 Karlsruhe 1

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Abstract

By electron beam treatment of flue gases, NO_x and SO_2 are converted to nitric and sulfuric acids simultaneously. Upon ammonia addition, the corresponding salts are collected in solid state and can be sold as fertilizer. Both homogeneous gas phase reactions and physico-chemical aerosol dynamics are involved in product formation. These processes have been analyzed by model calculations.
In part I, the present report summarizes the model results and gives an account of the theoretical understanding of the EBDS process and its performance characteristics.
Part II of this report gives a complete listing of the reactions used in the AGATE code.

Reaktionskinetik der Rauchgasreinigung durch Elektronenstrahl

Übersicht

Bei der Bestrahlung von Rauchgasen mit Elektronen werden NO_x und SO_2 simultan zu Salpetersäure bzw. Schwefelsäure oxidiert. Durch Ammoniakzugabe entstehen die entsprechenden Salze in fester Form; sie können abfiltriert werden und sind als Düngemittel verkäuflich. An der Produktbildung sind homogene Gasphasenreaktionen und physikalisch-chemische Aerosolprozesse beteiligt.
In Teil I dieses Berichts werden die Ergebnisse der Modellrechnungen zusammengefaßt. Dabei werden die Grundlagen und Anwendungscharakteristiken des Elektronenstrahlverfahrens diskutiert.
Teil II gibt eine Liste der im AGATE-Code benutzten Reaktionen.

Part I

Chemical Kinetics of Flue Gas Cleaning by Electron Beam

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1. Introduction

NO_x and SO_2 emissions from fossile fuel burning power plants have been recognized as sources of atmospheric and biospheric hazards. Their avoidance is being forced presently. Existent pollutant control technologies solve this task mostly in two stages which reduce NO_x and SO_2 emissions separately, yielding economically unimportant products like N_2 and $CaSO_4$. The EBDS (Electron Beam Dry Scrubbing) process offers an economic alternative: the irradiation of the flue gas with fast (300 - 800 keV) electrons initiates the build-up of radical concentrations which are high enough to oxidize NO_x and SO_2 traces simultaneously. Only a minor portion of the nitrogen oxides is transformed to molecular nitrogen and dinitrogen oxide. The oxidation products are nitric and sulfuric acids. Ammonia addition induces the formation of a mixed ammonium nitrate/sulfate aerosol which can be collected as solid and sold as fertilizer.

Originally developed in Japan (e.g. Tokunaga et al., 1978, 1984; Suzuki et al. 1981), the EBDS process has been promoted in the US and West Germany (e.g. Frank et al., 1985, 1988; Jordan, 1988) and has gained international recognition (Markovic, 1987). Detailed model studies have provided much insight into the chemical kinetics of the process (e.g. Nishimura et al., 1979, 1981; Person et al., 1985, 1988; Busi et al., 1987, 1988; Gentry et al., 1988), although some unresolved questions are left.

The EBDS process involves very different physico-chemical steps like energy absorption, reactions in homogeneous gas phase and heterogeneous aerosol particle and mass growth. Energy absorption produces chemically active species at concentration levels which represent a highly unstable state compared to thermal equilibrium. In this sense irradiation by e-beam invokes a sudden deviation from thermodynamic equilibrium in the waste gas. Subsequent relaxation establishes a new equilibrium state which is characterized by lower NO_x/SO_2 concentrations and aerosol formation. A theoretical description of this relaxation process is hardly possible by simple thermodynamics, but requires the use of appropriate kinetic models. The AGATE-code has been developed for this purpose and the present study is widely based on its results as well as their analysis.

The goal of this study is to show how microscopic molecular interactions work together and determine the characteristics, performance and thereby the economics of the EBDS process. After a short description of the primary radiolytic events, the chemistry of the primary active species is considered. The reactions of positive ions are shown to constitute the major source of neutral radicals. These radicals are needed to convert NO_x to nitric acid and SO_2 to sulfuric acid. The OH radical turns out to be the most important radical for the formation of these acids and hence the final nitrate/sulfate aerosol. In addition, nitric acid is also produced directly from some ion-molecule reactions which work most efficiently at high concentrations of water vapour.

The oxidation of NO_x by radicals is not a simple straightforward reaction sequence, however. Part of the intermediate NO_2 is reduced back to NO by oxygen atoms. Further, intermediate HNO_2 is likely to decompose at surfaces, which acts as an OH sink. Such "back-reactions" determine the dose dependence of NO_x removal and thereby the economics of the EBDS process. Other reductive pathways yield N_2O as gaseous by-product and also molecular nitrogen. The nitrogen formation is not easy to measure and therefore, the N balance is difficult to investigate experimentally.

The added ammonia partly enters into the radiation induced radical chemistry. It favours the reduction of NO to N_2 and of NO_2 to N_2O. The reactions behind are similar to those of the thermal $DeNO_x$ process.

The major part of the ammonia, of course, is consumed for ammonium salt formation. Ammonia thus provides a link between gas phase chemistry and particulate formation. The properties of the developing aerosol are investigated and heterogeneous reactions at the aerosol surface are discussed.

All these physico-chemical mechanisms work together simultaneously. Kinetic models allow to quantify the net effects of single mechanisms or reactions separately and to assess their contributions and importance for the entire process. This reveals the molecular interactions which are responsible for the measurable performance characteristics of the EBDS process, like dose dependence of removal yields and product formation or relative humidity effects, for instance.

Many results described in part I of this report have been obtained from the AGATE-code. A complete listing of the reaction set is given in part II.

2. Radiolysis

2.1. The fate of fast electrons

The interaction of electrons with matter depends both on the electron energy and certain target properties. In the EBDS process, the energy of incident electrons is in the range 300 keV - 800 keV typically. This energy is too low to permit close electron-nuclei interactions, the origin of Bremsstrahlung.

Rather, the incident electrons transfer part of their energy to the electron shells of molecules by inelastic collisions. These collisions are also associated with momentum transfer and the electrons are readily scattered throughout the irradiated medium. A full description of the energy release by accelerated electrons is fairly complicated (Meissner, 1964) and the history of an individual electron is only accessible by numerical methods. Therefore, integral values have gained practical importance. One example is the so-called linear energy transfer (LET). It is defined as the energy of the incident electron divided by its total pathlength in the traversed medium (Henglein et al., 1969). The LET depends mainly on the electron energy and the density of the medium, but also on its chemical composition (Lohrmann, 1983). For 300 keV electrons in liquid water, the LET is of the order of 0.5 eV/nm; in air at ambient conditions it is roughly a factor of 1,000 lower. The LET gives an idea of the electron range R, although in a rigorous sense, these values are not related. The electron range may be defined as the linear distance from the source at which the average electron energy has decayed to 1 - 5% of the start value. The accuracy of this definition is subject to practical requirements (Henglein et al., 1969). For 300 keV electrons in air at NTP, R is approximately 0.5 m. Also, it is reasonable to assume $R \sim \rho \cdot E^{1.35}$, where ρ is the material density and E the incident energy between 300 keV and 800 keV (Landolt-Börnstein, 1952; Lohrmann, 1983).

The energy loss in single collisions varies statistically between a few eV ("distant collisions") and some tens of keV ("close collisions"). Both of these extremes are comparatively scarce and leave the contact molecules in excited states or as (excited) ions, respectively. In the latter case, secondary electrons with a kinetic energy of many keV may be produced, which may cause further ionization themselves. In this way, tertiary and higher order electrons result from ionization processes, which all contribute to the spatial energy distribution initiated by the primary electrons. The overall gain of excited state molecules, direct dissociation into neutral radicals and dissociation into ion pairs is described by G-values (Willis et al., 1976). These G-values are an average over the combined effects of all orders of electrons. The ionization gain is about three ion pairs per 100 eV absorbed energy in air. It is fairly independent of primary electron energy, but may depend on the dose rate (Willis et al., 1976; Armstrong, 1987).

The EBDS processing of waste gases typically involves dose rates below about 1000 kGy/sec, which is a much lower dose rate than may be obtained in Febetron studies. Among others, this comparison has given rise to the question, if the performance of the EBDS process depends on the dose rate. Many different aspects are related to this subject and will be discussed throughout this paper. At this stage, it is only considered in terms of energy deposition.

The microscopic time scale of the energy transfer can be estimated from the classical mechanics of elastic collisions neglecting the kinetic energy loss by electron-molecule interaction. As an upper limit, collision times of the order of 10^{-16} sec are obtained for an energy transfer of some 10 eV to a single molecule by an electron of several hundred keV incident energy (Armstrong, 1987). This is by far the shortest time scale of any physico-chemical process involved in EBDS and it is definitely beyond the scope of technical process control means. Interestingly, this corresponds to a microscopic dose rate around $3 \cdot 10^{21}$ kGy/sec for molecular weights $\approx$ 30 g/mol. Obviously, such processes are well beyond the scope of process control.

2.2. The fate of primary species

Turning back to macroscopic considerations, molecular excitation, homolytic dissociation and ionization are counteracted by quenching, radical recombination and associative ion-electron recombination, respectively. The first two "deactivation" processes are not directly related to the energy absorption and will be discussed later. Ion-electron recombination can occur only when the electrons have "cooled" down to thermal energy ($kT \approx 0.01$ eV at 273 K). Thermalization takes about 1 nsec in air at 1 atm (Armstrong, 1987). During this time, the primary ions may already undergo charge transfer reactions or attach to neutral molecules and form ionic clusters. Due to Brownian motion, the positive charge (i.e. a single or clustered ion) diffuses a linear distance of about 0.1 µm at NTP in the absence of external force fields. This range may be imagined as a spherical ion core, which develops around the ionization point prior to charge neutralization.

Both charge transfer and dissociative neutralization reactions produce radicals. As will be shown below, the life time of radicals is at least 10 nsec and the quenching of excited transients takes 200 nsec on the average. The diffusive motion of these species constitutes a chemical core about the point of electron impact, which is in the µm-range. According to common terminology, this is called a spur. Along the path of energetic electrons, spurs are created "like beads on a string" (Chatterjee, 1987). The entity of spurs represents the electron track as observed in cloud chambers.

An overlap of spurs (and hence tracks) generated by different electrons can be expected to favour the recombination of active species by a local increase of their concentrations above the normal level of independent energy transfer events. Also, the chemical mechanism may change in this way, e.g. through preference of alternative reaction branches. This effect has been accepted to explain the dose rate dependent ozone formation in the radiolysis of pure oxygen (Sauer, 1976). The dose rate, at which spur overlap occurs, can be estimated from the G-value for ionization, the spur dimension and its evolution time. Using the figures given above, one obtains

$$\dot{D} \approx \frac{(100/3)\,eV}{(5\ \mu m)^3 \cdot 10^{-8} sec} \approx 2 \cdot 10^{19} \frac{eV}{cm^3 \cdot sec} = 5 \cdot 10^3 \frac{kGy}{sec}$$

for air or waste gas conditions. This rough estimate for the onset of dose rate effects is in accordance with recent model calculations on the EBDS process (Gentry et al., 1988). Also it is well above the dose rates obtained with presently available electron accelerators in waste gas treatment. A necessary minimum dose rate for the onset of measurable radiation effects will be discussed in section 3.4.

3. Gas phase chemistry: excited species, primary radicals and ions

Since its discovery in the early 1970's, the characteristics of the EBDS-process have been discussed in terms of the chemical reactions in homogeneous gas phase, which precede and induce particulate formation (e.g. Nishimura et al., 1979, 1981). During the past decade, the discussion has been stimulated through the development of extensive computer codes on this part of the process (Busi et al., 1988; Person et al., 1988; Mätzing, 1988). The results of these modeling studies provide an understanding of most experimental findings. A summary is given below and an interpretation of the various reaction types is offered.

3.1. Modeling active species generation

A microscopic modeling of energy absorption and active species generation, e.g. by Monte Carlo methods, has not been attempted in EBDS-models. Rather, integral descriptions of the primary processes are in use, which relate active species formation directly to the dose rate experienced by flue gas:

$$\frac{dn}{dt} = G_n \cdot \dot{D} \cdot x_i \cdot \rho$$

In this basic equation, n is the number concentration of species n, generated from species i with mole fraction x_i in the flue gas. G_n is the corresponding gain [molecules/100eV], as discussed above (for details see Klassen, 1987; Armstrong, 1987). $\dot{D} \cdot \rho$ is the dose rate times the average density in units of 100 eV/cm^3 • sec.

Two basic assumptions are inherent in this equation:

(i) energy absorption can be treated as a quasi-continuous process, and

(ii) the probability of electron impact is proportional to the (mass) concentration of the parent species.

The first assumption is applicable, because only low LET electrons are considered, and is supported by the dose rate consideration in the preceding chapter. The second assumption regards the collisional cross-section for electron-molecule interaction as independent of electron energy and molecule nature. This is valid for electron energies down to about 30 keV (e.g. Cole, 1969) and hence over at least 90% of the electron range.

Assumption (ii) also suggests to neglect radiolytic degradation of trace constituents in the flue gas and to regard only the major components in energy absorption. From the G-values reported by Willis and Boyd (1976) the relevant stoichiometric equations read:

$$\begin{aligned} 4.43\,N_2 \quad & \xrightarrow{100\,\mathrm{eV}} 0.29\,N_2^* + 0.885\,N\,(^2D) + 0.295\,N\,(^2P) \\ & \quad + 1.87\,N\,(^4S) + 2.27\,N_2^+ + 0.69\,N^+ + 2.96\,e^- \end{aligned}$$

$$\begin{aligned} 5.377\,O_2 \quad & \xrightarrow{100\,\mathrm{eV}} 0.077\,O_2^* + 2.25\,O\,(^1D) + 2.8\,O\,(^3P) \\ & \quad + 0.18\,O^* + 2.07\,O_2^+ + 1.23\,O^+ + 3.3\,e^- \end{aligned}$$

$$\begin{aligned} 7.33\,H_2O \quad & \xrightarrow{100\,\mathrm{eV}} 0.51\,H_2 + 0.46\,O\,(^3P) + 4.25\,OH + 4.15\,H \\ & \quad + 1.99\,H_2O^+ + 0.01\,H_2^+ + 0.57\,OH^+ + 0.67\,H^+ \\ & \quad + 0.06\,O^+ + 3.3\,e^- \end{aligned}$$

$$\begin{aligned} 7.54\,CO_2 \quad & \xrightarrow{100\,\mathrm{eV}} 4.72\,CO + 5.16\,O\,(^3P) + 2.24\,CO_2^+ \\ & \quad + 0.51\,CO^+ + 0.07\,C^+ + 0.21\,O^+ + 3.03\,e^- \end{aligned}$$

This representation implies some simplifications concerning the nature of electronically excited nitrogen and oxygen molecules. Dissociative states have been treated as forming atoms directly. Therefore, N_2^* and O_2^* represent the sum of all long-lived excited state molecules described by Willis and Boyd (1976). In the present context, it is reasonable to treat these as $N_2(A)$ and $O_2(^1\Delta_g)$: The numerical results do not change upon variation of the corresponding G-values by a factor of ± 2 (Mätzing, 1987 a). O^* denotes a highly excited O atom above the $O(^1S)$ level.

3.2. Reactions of primary excited species

Electronically excited state species arise only from nitrogen and oxygen radiolysis. Those considered here have radiative life times above 1 µsec. The rate constants for collisional quenching are less than 10^{-14} $cm^3 \cdot sec^{-1}$ (Baulch et al., 1980, 1982, 1984), which also gives life times above 1 µsec at 1 atm, $T \approx 350$ K. Compared to quenching rates, chemical reaction rates are 50 times faster typically. The reactions of excited state species with the main constituents of the flue gas therefore take place at a time scale of some hundred nsec , which exceeds electron thermalization times by two orders of magnitudes. So within 200 nsec they can diffuse over a linear distance up to 3 µm from their point of origin, before they are consumed ($D \approx 0.2$ cm^2/sec). This range determines the spur size within which all other reactions occur.

The total gain of excited state species can be estimated from the data in section 3.1 and is around 2 per 100 eV. The products of their reactions with the major waste gas constituents are H, N and O atoms and in particular, only little OH.

Excited species can thus initiate partial NO oxidation to NO_2. Thereafter, reduction reactions become important, yielding NO and N_2O from NO_2, and N_2 from NO. In this way, primary excited species lead to an oxidation-reduction cylce between NO and NO_2, which offers stable exit paths to gaseous products only. Nitric and also sulfuric acid are not formed due to the lack of sufficient OH concentrations. Particulate formation therefore cannot be expected to originate from the generation of excited species.

3.3. Reactions of primary radicals

According to the above given radiolytic equations, the total radical gain, ΣG (ground state radicals), is about 3 per 100 eV for a typical flue gas containing 75% N_2, 5% O_2, 10% H_2O and 10% CO_2. This gives a total radical production around $2 \cdot 10^{15}$ $cm^{-3} \cdot sec^{-1}$ at 10 kGy/sec under typical conditions. Consider typical termolecular recombination rate constants around $5 \cdot 10^{-33}$ $cm^6 \cdot sec^{-1}$ and an overall concentration of $2 \cdot 10^{19}$ molecules/cm^3. The quasi-stationary radical concentration is then given by

$$[Radical] = \left(\frac{2 \cdot 10^{15}}{5 \cdot 10^{-33} \cdot 2 \cdot 10^{19}}\right)^{1/2} cm^{-3} \approx 10^{14} \ cm^{-3}$$

On the one hand, this result shows that recombination cannot compete with primary radical production for dose rates $\leqq$ 10 kGy/sec. However, the kind of primary radicals is not much different from those originating from excited species. The primary OH formation from water vapour is not high enough to break the oxidation-reduction cycle between NO and NO_2 and to produce nitric acid effectively. The latter holds for sulfuric acid also. So for the same reasons as above, primary radical formation plays a minor part for NO_x/SO_2-removal in the EBDS process.

The radical levels discussed above are some orders of magnitude higher than those observed under tropospheric or stratospheric conditions (Levine, 1985). Therefore, a simple negation of their significance for NO_x/SO_2 degradation may not readily be accepted. Rather, one likes to expect the establishment of self-sustaining reaction chains which reinforce single steps. Chain lengths of the order of 10^3 ... 10^6 are not unusual in gas-phase or liquid-phase chemistry and would be sufficient in the present context.

In the low temperature NO_x-chemistry, such radical chains do not exist, however. One reason is the nature of the envisaged product (acid) formation:

Nitrous and nitric acids can only be formed via radical addition (OH, NO_3) to NO or NO_2. Those termolecular reactions can be considered as "terminating" steps, because NO and NO_2 are of radical nature themselves. A more careful investigation of bimolecular NO_x-radical reactions further shows that they can at best generate OH and O in the temperature range of interest here. The OH-radical can be consumed by recombination with NO_x, while O-atoms effectively counteract oxidative pathways via $NO_2 + O \rightarrow NO + O_2$ (see below).

Chain reactions in the H - C - O subsystem also must be excluded in this context, mainly because some of the propagating steps have high activation energies, but also because of depletion of radical concentrations by interactions with the N-O subsystem. Further, there are only very few SO_x-reactions possible in homogeneous gas phase under waste gas conditions and these do not support any chain reaction.

From these arguments it is understood that the primary radicals formed by e-beam irradiation of flue gas constitute only a very limited potential for NO_x/SO_2 degradation. By analogy, the same is recalled for excited species formation.

3.4. Reactions of primary ions

The above discussion leaves the key part of the EBDS chemistry to ionic processes. Among these, charge transfer reactions (whether dissociative or not) predominate: They proceed with rate constants around $5 \cdot 10^{-10}$ cm^3/sec at total molecule concentrations near $2 \cdot 10^{19}$ cm^{-3}, which corresponds to individual ion life times of only some 10^{-10} sec. Positive charge transfer reactions are ten times as fast as electron thermalization (see above) and every positive charge can be distributed freely among ten individual molecules, before the onset of charge neutralization reactions. A positive charge, which is created in an environment of already thermalized electrons, has a 10^7 times greater chance to react with surrounding neutral species than with negatively charged species because of concentration differences (10^{19} neutrals against 10^{12} negative charges). Vice versa, the same holds for the reactions of thermalized electrons which statistically rather recognize a neutral environment than positive charges in their neighbourhood. Yet, because neutralization reactions have about 10^3 times higher rate constants than ion-molecule reactions, the afore mentioned probability ratio is reduced from $10^7:1$ to $10^4:1$.

These figures, of course, must be regarded as rough estimates with an accuracy around an order of magnitude. Still they clearly demonstrate the preference of ion (electron) -neutral reactions over ionic recombination. In contrast to reactions of excited species and radicals, ion (electron) -molecule reactions naturally do not consume active species, but stabilize the charge separation initiated by e-beam treatment. It is therefore plausible to regard positive and negative ion chemistry as essentially independent or decoupled reactive pathways.

A true distinction of primary ion reactions from higher-order ion reactions, however, is neither possible nor meaningful, because the concentration of any charged species must be expected both to decay and to grow simultaneously due to charge transfer. It is obviously impossible to discriminate between primary O_2^+ ions and those who have got their charge from N_2^+, CO_2^+ or any other candidate, for example. So, the ionization yields reported above loose their "fingerprints" in the irradiated gas upon the onset of charge transfer reactions. This also means that charge transfer reactions re-distribute the incident energy consumed in primary ionization processes.

For the subsequent discussion of the ion chemistry, it is interesting to estimate the total ionization level established in irradiated waste gas. The quasi-stationary ion concentrations are given by

$$\frac{dn_+}{dt} = \frac{dn_-}{dt} = G_{ion} \cdot \dot{D} \cdot \rho - k_{rec} \cdot n_+^2 \approx 0$$

where $n_+ = n_-$ are the number concentrations of all positive or negative species respectively. $G_{ion} \approx 3$ per 100 eV is the average ionization gain in the gas, $\dot{D}$ is the dose rate and $\rho \approx 1$ kg/m³ is the gas density. The mutual recombination rate constant is $k_{rec} \approx 10^{-7}$ cm³/sec. For $\dot{D} = 10$ kGy/sec this gives $n_+ = n_- \approx 10^{10}$ cm⁻³, which is about 10^6 times higher than typical tropospheric ionization levels (Levine, 1985; Friedlander, 1977). Since the quasi-stationary charge concentrations are approximately proportional to the square root of dose rate, the dose rate must be greater than about 10^{-10} kGy/sec for the ionization level to exceed the natural background. This extremely small value gives the minimum dose rate required for the onset of observable radiation effects and sets some kind of a physical lower limit, at which dose rate effects can be expected. Certainly, such a figure has no technical relevance.

3.5. Positive ion chemistry

The charge transfer processes lead the way from comparatively unstable and short-lived ions to more stable ions and ionic clusters with longer life times. Among the primary molecular ions, O_2^+ and H_2O^+ must be considered more stable than N_2^+ and CO_2^+, which is demonstrated by the reaction sequence

$N_2^+ + O_2 \rightarrow O_2^+ + N_2$ $k_1 = 3.9 \cdot 10^{-10} \cdot \exp(-T/143)$ cm³/sec

$N_2^+ + CO_2 \rightarrow CO_2^+ + N_2$ $k_2 = 8.3 \cdot 10^{-10}$ cm³/sec

$CO_2^+ + O_2 \rightarrow O_2^+ + CO_2$ $k_3 = 6.5 \cdot 10^{-9} \cdot T^{-0.78}$ cm³/sec

$N_2^+ + H_2O \rightarrow H_2O^+ + N_2$ $k_4 = 2 \cdot 10^{-9}$ cm³/sec

$CO_2^+ + H_2O \rightarrow H_2O^+ + CO_2$ $k_5 = 1.7 \cdot 10^{-9}$ cm³/sec

$H_2O^+ + O_2 \rightarrow O_2^+ + H_2O$ $k_6 = 2.6 \cdot 10^{-10}$ cm³/sec

The corresponding reverse reactions are negligible (Anicich et al., 1986), which is characteristic for this reaction type (at temperatures around 100 °C).

Charge transfer reactions which re-generate N_2^+ or CO_2^+ do not compete with primary ionization under usual conditions. Hence, considering N_2^+ as illustrative example, its quasi-stationary concentration can be estimated from

$$\frac{d[N_2^+]}{dt} \approx G_{N_2^+} \cdot \dot{D} \cdot \rho \cdot x_{N_2} - k_{tr.} \cdot [N_2^+] \cdot n - k_{rec} \cdot [N_2^+] \cdot n_- \approx 0$$

Here, k_{tr} is the rate constant for the charge transfer reactions, n is the concentration of reactant neutrals and the other symbols have the same meaning as above.

From the preceding section n_- is known to be

$$n_- \approx \sqrt{G_{ion} \cdot \dot{D} \cdot \rho / k_{rec}}$$

so that

$$[N_2^+] \approx \frac{G(N_2^+) \cdot \dot{D} \cdot \rho \cdot x_{N_2}}{k_{tr} \cdot n + \sqrt{G_{ion} \cdot \dot{D} \cdot \rho \cdot k_{rec}}} \approx \frac{10^{15}}{4 \cdot 10^9 + 10^4} cm^{-3}$$

The figures hold for the typical waste gas conditions mentioned above; in particular $x_{N_2} \approx 0.75$, $k_{tr} \approx 10^{-9}$ cm³/sec, $k_{rec} \approx 10^{-7}$ cm³/sec and $\dot{D} = 10$ kGy/sec. The example is not meant to stress absolute figures, but to point out

(i) rapid charge transfer makes many ion concentrations proportional to the dose rate,

(ii) charge transfer usually is many orders of magnitude faster than ion neutralization.

Again, this supports the above conclusion on the negligible significance of dose rate effects. But also, reactive pathways must be supposed closely related to the dose rate, just like the ion concentrations.

The key to this relation is obtained from a consideration of dissociative reactions which conserve the total ion concentrations and produce radicals, e.g.

$$O_2^+(H_2O) + H_2O \rightarrow H_3O^+ + OH + O_2 \qquad k_7 = 2 \cdot 10^{-10} \text{ cm}^3/\text{sec}$$

Due to the essential quasi-stationarity of ion concentrations, reactions like these constitute a quasi-continuous radical source. Using $[H_2O] = 10^{18}$ cm^{-3} (≈ 5 vol.%) and $[O_2^+(H_2O)] = 10^6$ cm^{-3} (i.e. in the range for $[N_2^+]$ like above) one obtains

$$\frac{d[OH]}{dt} \approx 2 \cdot 10^{-10} \cdot 10^{24} cm^{-3} \cdot sec^{-1} \approx 10\, ppm/sec$$

at $\dot{D} = 10$ kGy/sec for the OH production rate due to reaction (7). The branching reaction (7.a)

$$O_2^+(H_2O) + H_2O \rightarrow H_3O^+(OH) + O_2 \qquad k_{7a} = 1.5 \cdot 10^{-9} \text{ cm}^3/\text{sec}$$

is roughly ten times faster than reaction (7) and is followed by the detachment reaction

$$H_3O^+(OH) + H_2O \rightarrow H_3O^+ + OH + H_2O \qquad k_8 = 1.4 \cdot 10^{-9} \text{ cm}^3/\text{sec}$$

These sequences lead to OH production rates of the order of 100 ppm/sec at $\dot{D} = 10$ kGy/sec. This obviously is the magnitude of radical production rates required for effective process performance. In analogy, other radicals are produced from:

$$N^+ + H_2O, CO_2, O_2 \rightarrow N + H_2O^+, CO_2^+, O_2^+$$

$$O^+ + O_2, N_2 \rightarrow O + O_2^+, N_2^+$$

$$H^+ + O_2, H_2O, CO_2 \rightarrow H + O_2^+, H_2O^+, CO_2^+$$

The above example has thus revealed charge transfer processes as the major radical source. Like the parent ion concentration, radical production rates are therefore proportional to dose rate. Consequences thereof will be discussed later.

3.6. Negative ion chemistry

It has been pointed out earlier that the negative ion chemistry occurs somewhat delayed compared to positive ion chemistry, because the time required for electron thermalization (≈ 1 nsec) is about ten times longer than the characteristic time scale for (positive) ion-molecule reactions. The principal reactions of thermalized electrons are those of termolecular attachment, leading to O_2^-, , NO_x^- and other negative ions as well as to the corresponding ionic clusters. In analogy to the preceding chapter, one might expect another radical source to originate from negative ion chemistry. This is not the case, however: Negative ion-molecule reactions do not release radicals as "byproducts". This particular property makes negative ion chemistry a fairly unimportant sideway in the EBDS process. Arguments in favour of relatively stable negative ions like NO_2^- and NO_3^- do not hold, because these are not at all liable to enter into the particulate phase; rather, they re-generate NO_x by charge neutralization. The author has tested the effect of negative ion chemistry by tentative omission from his computer model: Compared to the full mechanism, the calculated final removal efficiencies for NO_x and SO_2 changed by less than 1 ppm which is below any realistic detection limit (Mätzing, 1987 a).

3.7. Ion mutual neutralization

Ionic recombination is of course the final fate of the charge separation initiated by impact of high energy electrons with molecules. It is therefore a necessary condition for the degradation of the absorbed energy which leads to the final new equilibrium state of the cleaned waste gas. Yet, for the degree of contaminant removal, ionic recombination is totally unimportant, as has been argued throughout this discussion and especially in the preceding chapter.

3.8. Overview on the chemistry of primary species

The irradiation by electron beam results in the direct formation of the following primary reactive species:

(i) excited molecules

(ii) radicals in ground and excited states

(iii) positive ions.

Negative ions are formed from attachment of thermalized electrons to neutral species.

The primary neutral reactants (i) and (ii) do not bring about substantial NO_x/SO_2 oxidation, mainly because of their inability to initiate significant OH formation. The OH radical is needed for nitric and sulfuric acid formation.

The positive ions undergo fast charge transfer reactions in which radicals are formed as "byproducts". This constitutes the major radical source and in particular the only significant OH source in the EBDS process. In contrary, the chemistry of negative ions does not contribute to radical formation nor to NO_x/SO_2 degradation.

4. Gas phase chemistry: Positive ions and radicals

So far, the absorption of high energy electrons in waste gases have been discussed, the formation of primary species and their relevance for contaminant removal. The major radical source has been shown to originate from positive ion chemistry in the gas phase. Still it would be too simplified to regard positive ion-molecule reactions solely under the aspect of radical formation. In fact, they must also be considered as oxidizing reactions. Therefore, their role in contaminant removal cannot strictly be separated from the role of radicals, hence these mechanisms are discussed together under the same heading.

4.1. NO_x-oxidation by positive ions

From the generalized theory of redox processes it is well known that electron uptake constitutes the transition to a lower oxidation state. Hence, aquirement of a positive charge (i.e. release of an electron) is synonymous with oxidation.
Primary ionization can be interpreted in this way. Subsequent charge transfer processes can also be regarded as redox processes. While in the preceding chapters only the major constituents of the waste gas have been considered, the focus is now on the fate of trace contaminants. Charge transfer to trace species proceeds at a 1000 times longer time scale (i.e. $\approx 10^{-7}$ sec) than charge transfer to major components, simply because of the difference in concentration. The most important waste gas contaminants are NO and SO_2, which can readily be oxidized to NO^+ and $SO_2{}^+$. Of course, these ions again are liable to loose their charge to neighbouring neutrals and this is the simple fate of $SO_2{}^+$ (Anicich et al., 1986). But the chemistry of NO^+ offers an important alternative: NO^+ stabilizes through the attachment of one, two or three water molecules (Fehsenfeld et al., 1971; Sutherland et al., 1975). As the $NO^+(H_2O)$ associate can be imagined as a mesomeric form of protonated nitrous acid, it appears very natural that NO^+-H_2O clusters can release nitrous acid. It is the merit of Fehsenfeld et al. (1971) who pointed out this analogy between gas phase and aqueous phase ion chemistry. Hence the oxidation of NO to NO^+ eventually becomes manifest through

$$NO^+(H_2O)_3 + H_2O \rightarrow HNO_2 + H_3O^+(H_2O)_2$$

$$k_9 = 2 \cdot 10^{-6} \cdot \exp(-3000/T) \text{ cm}^3/\text{sec}$$

which is only slightly opposed by the reverse reaction, $k_{-9} = 1.1 \cdot 10^{-8} \cdot (300/T)^{2.6}$ cm³/sec (Fehsenfeld et al., 1971; Sutherland et al., 1975). This already provides an indication that nitrous acid must be expected to form from gas phase reactions. Nitrous acid is kinetically stable in the gas phase (eg. Vosper, 1976; Kaiser et al., 1977 b; Jenkin et al., 1987; Levine, 1985), which has particular consequences for the EBDS process to be discussed below.

4.2. Radical reactions

Positive charge transfer processes have been shown above to produce radicals at a rate of approximately 100 ppm/sec $\approx 2 \cdot 10^{15}$ cm^{-3} sec^{-1} at $\dot{D} = 10$ kGy/sec ($T \approx 350$ K, $P \approx 1$ bar). The radical production rate is essentially proportional to the dose rate. Bimolecular radical-radical reactions may both reduce the total radical concentration, e.g.

$$H + HO_2 \rightarrow H_2 + O_2$$
$$H + HO_2 \rightarrow H_2O + O$$

or keep it unchanged through formation of a new radical pair, e.g.

$$H + HO_2 \rightarrow 2\,OH$$
$$NH_2 + N \rightarrow N_2 + 2\,H$$

Termolecular radical recombination always depletes the available radical reservoir, the rate constants are of the order of $k_{ter} \approx 5 \cdot 10^{-33}$ $cm^6 \cdot sec^{-1}$, so that $k_{ter} \cdot [M] \approx 10^{-13}$ $cm^3 \cdot sec^{-1}$. As a careful overall estimate, radical recombination will be treated using a bimolecular rate constant of $5 \cdot 10^{-12}$ $cm^3 \cdot sec^{-1}$. For comparison, fast radical-molecule reactions proceed with equally high rate constants. Then, quasi-stationary radical concentrations [R] can be estimated from

$$\frac{d[R]}{dt} \approx 2 \cdot 10^{15} cm^{-3} \cdot sec^{-1} - 5 \cdot 10^{-12} cm^3/sec\,[R] \cdot n - 5 \cdot 10^{-12} cm^3/sec\,[R]^2 \approx 0$$

which gives radical levels in the ppb range for neutral concentrations $n \approx 10^{16} \dots 10^{19}$ cm^{-3} at $\dot{D} \approx 10$ kGy/sec. The already overestimated quadratic term above can be neglected ($n >> [R]$). This means:

(i) radical concentrations are proportional to the dose rate;

(ii) radical recombination becomes important only at high dose rates, definitely above 1000 kGy/sec.

These rough estimates have been confirmed by detailed modeling studies (Gentry et al., 1988) and again exclude any dose rate effect from the more chemical side of the process. This is also in agreement with the above discussed upper physical limit for the occurence of dose rate effects.

Concerning the fate of radicals, two termolecular reactions must be considered:

$$O + O_2 + M \rightarrow O_3 + M$$

$$H + O_2 + M \rightarrow HO_2 + M$$

These reactions proceed with rate constants $k \cdot [M] \approx 10^{-14}$ and $3 \cdot 10^{-12}$ cm^3/sec. respectively and thus make the hydroperoxide radical and ozone substantial oxidizers for NO. Thereby, NO_2 production is started. This results in a competition of NO, NO_2 and SO_2 for OH:

$$NO + OH + M \rightarrow HNO_2 + M \qquad k_{10} \cdot [M] \approx 4 \cdot 10^{-12} \; cm^3/sec$$

$$NO_2 + OH + M \rightarrow HNO_3 + M \qquad k_{11} \cdot [M] \approx 9 \cdot 10^{-12} \; cm^3/sec$$

$$SO_2 + OH + M \rightarrow HSO_3 + M \qquad k_{12} \cdot [M] \approx 7 \cdot 10^{-13} \; cm^3/sec$$

(Baulch et al., 1980, 1982, 1984).

The crucial importance of this competitive set of termolecular reactions for the EBDS process arises from the following arguments:

(i) reaction (12) is practically the only important SO_2 sink in homogeneous gas phase;

(ii) reaction (11) is the only important source of nitric acid from neutral reactants in homogeneous gas phase;

(iii) reaction (10) is a very effective NO sink, but leads only to gaseous nitrous acid which does not form an ammonium salt upon ammonia addition (Kaiser et al., 1978);

(iv) reaction (12) is followed by the fast reaction $HSO_3 + O_2 \rightarrow SO_3 + HO_2$ (Gleason et al., 1987) which immediately induces sulfuric acid formation and nucleation and simultaneously releases HO_2; its competition with reaction (10) is therefore desirable in that it both inhibits HNO_2 formation and supports the sequence

$$NO + HO_2 \rightarrow NO_2 + OH \xrightarrow{M} HNO_3$$

The last argument clearly stresses the option of simultaneous NO_x/SO_2 removal by EBDS and explains the increase of NO removal with increasing SO_2 concentration which has been observed by experiment (Paur et al., 1988 a).

Despite their basic importance, these considerations do not constitute the whole story: According to the above arguments, a kind of turnover would be expected at very high SO_2 concentrations in that they would promote NO_2 formation but also inhibit nitric acid formation by consumption of OH. In this case, NO_x removal would decrease with increasing sulfate formation. Such a turnover has never been reported from experimental investigations.

One explanation for this experimental gap certainly is the ionic pathway which also contributes to nitric acid formation from NO_2. This path is in perfect analogy to the ionic NO oxidation described above and the key reaction is

$$NO_2^+ (H_2O)_2 + H_2O \rightarrow HNO_3 + H_3O^+(H_2O)$$

(Fehsenfeld et al., 1975). Obviously and with appreciation, this ionic pathway prohibits the observation of the turnover suggested above, especially because the destruction of HNO_3 by thermal electrons, albeit fast, is of negligible importance in the present context (see Fehsenfeld et al., 1975).

A second and supplementary explanation stems from the observation that NO_2 (and NO) does not only enter into oxidation reactions but also into reduction reactions which are discussed below.

4.3. Oxidation versus reduction

It has been pointed out above that during irradiation of waste gas with energetic electrons NO is oxidized to NO_2 by O_3 and HO_2. Termolecular oxidation of NO by O atoms and oxidation by molecular oxygen are too slow for a process which must be finished at a time scale of a few seconds or less. NO oxidation and nitric acid formation have also been shown to be supported by sulfur dioxide. In this section, the focus is on reductive pathways which may both favour and oppose NO_x degradation and certainly do not support nitrate formation.

Neglecting negatively charged species, H and N atoms are favourite candidates to invoke reductive pathways. The fastest radical reaction is

$$N + NO \rightarrow N_2 + O \qquad k_{13} = 3.25 \cdot 10^{-11} \text{ cm}^3/\text{sec}$$

(Baulch et al., 1983; Brown et al., 1979). In this reaction, nitric oxide is reduced to molecular nitrogen, which is a welcome product. Under typical conditions, roughly 10% of the NO are removed in this way (Baumann et al., 1987). The molecular nitrogen can be detected only by sophisticated analytical methods which are not commonly in use. Most often, the N balance is based on NO_x input and output measurements including product nitrate. The thus observed deficiency in the N balance has first been explained by model calculations in terms of undetected molecular nitrogen. It will be shown in chapter 5 that additional molecular nitrogen is formed from ammonia oxidation and NO reduction. Note that in the above reaction 13 an oxygen atom is released, which is a really unfavourable intermediate, as shown below.

The reduction of NO_2 by N atoms has been discussed in terms of the following reaction branches:

$$
\begin{aligned}
NO_2 + N &\rightarrow 2\,NO \\
&\rightarrow O_2 + N_2 \\
&\rightarrow N_2O + O
\end{aligned}
$$

It is well established that the reaction takes the last branch exclusively (Baulch et al., 1984) thus producing N_2O as stable product and also an intermediate O-atom. Up to a dose around 10 kGy, the N_2O production from this reaction is only a few ppm, since the N atoms are consumed preferentially by NO.

Fortunately, the reaction $N + O_2 \rightarrow NO + O$ has too high an activation energy to be important in the temperature range around 100 °C (Baulch et al., 1980).

The oxygen atoms attach to molecular oxygen only comparatively slowly (see above). Instead, they effectively reduce NO_2 to NO:

$$NO_2 + O \rightarrow NO + O_2 \qquad k_{14} = 5.2 \cdot 10^{-12} \cdot \exp(+200/T)\ cm^3/sec$$

(Geers-Müller et al., 1987). This unfortunate reaction opposes NO oxidation extensively. Reaction (14) has been shown to account for the nonlinear NO-removal as function of dose (Mätzing, 1989).

Also, it can be used to estimate intermediate O atom concentrations from measured NO vs. dose curves. One goal for optimum process performance therefore should be to suppress reaction (14) by offering alternative reaction paths to NO_2 or O or both.

The H atoms mentioned above preferably attach to molecular oxygen thereby forming HO_2 (see above) which is needed for NO oxidation. Part of the HO_2 (and also of OH) recombines under formation of H_2O_2 and this recombination is favoured by high concentrations of water vapour. H_2O_2 is comparatively stable under typical EBDS conditions and has a vapour pressure low enough to suggest its condensation at the particulate surface. Its calculated final concentration is around 20 ppb (Mätzing, 1987a).

To a minor extent, H atoms also reduce NO_x:

$$NO_2 + H \rightarrow NO + OH \qquad k_{15} = 5.8 \cdot 10^{-10} \cdot \exp(-740/T)\ cm^3/sec$$

$$NO + H + M \rightarrow HNO + M \qquad k_{16} \cdot [M] \approx 10^{-13} \cdot \exp(+300/T)\ cm^3/sec$$

(Baulch et al., 1983). While reaction (15) may be interpreted to favour nitrous acid formation, reaction (16) rather favours nitric acid formation via

$$HNO + O_2 \rightarrow HO_2 + NO \quad k_{17} = 3.3 \cdot 10^{-14}\ \mathrm{cm^3/sec}$$

$$\rightarrow OH + NO_2 \quad k_{18} = 1.7 \cdot 10^{-15}\ \mathrm{cm^3/sec}$$

(Hack et al., 1985a, b)

But altogether, the interaction of H atoms with NO_x is of minor importance.

It has now become clear that NO_x oxidation is partly complemented by NO_x reduction through N_2 and N_2O formation. However, reductive pathways also oppose oxidative reactions in a way to decrease the removal efficiency with rising dose. Thus, NO_x removal is a nonlinear function of dose and eventually attains a saturation with increasing dose.

Therefore, it has been attempted to substitute a single, high dose irradiation step by successive low dose irradiation steps in order to save energy and increase efficiency. The results show that multiple irradiation may in fact increase the NO_x removal efficiency (Baumann et al., 1987).

The above discussion suggests multiple irradiation to be most effective, if NO_2 is removed between successive irradiation steps thus preventing its late reduction to NO.

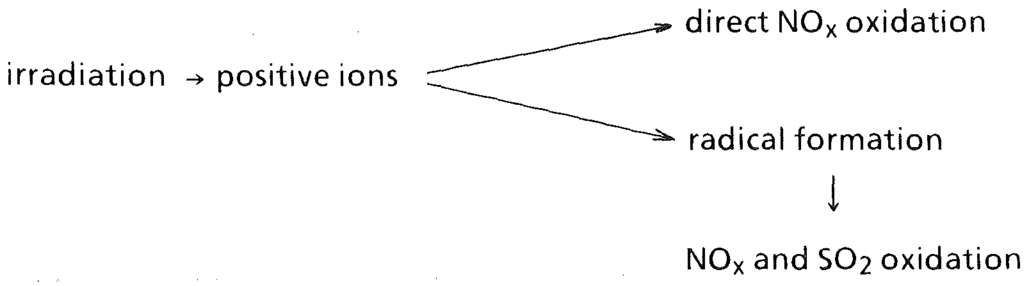
The nonlinear dose dependence of NO_x removal has also given rise to the study of dose rate effects in the EBDS process (Wittig et al., 1988a, b). In fact, both ion and radical formation rates are proportional to the dose rate, as shown above. Since mutual recombination of ions and radicals are comparatively slow at $\dot{D} \leqq 1000$ kGy/sec, the active species concentrations are proportional to the dose rate. Hence the overall chemical reaction proceeds the faster, the higher the dose rate. This holds for both the oxidative and reductive pathways described above. Therefore, rising dose rate accelerates every single reaction step involved in the decay of the irradiated gas mixture from its non equilibrium state to its new equilibrium state. The low density and viscosity of the waste gas under consideration also prohibit local overheating by high dose rates and thus prevent changes of the chemical mechanism. So the final gas composition depends only on the initial deviation from equilibrium, i.e. on the absorbed dose, and not on "pulse intensity", i.e. dose rate. This has been shown to be valid for dose rates less than about 1000 kGy/sec (Gentry et al., 1988).

It must be added that this is often interpreted from the point of constant acceleration voltage which for present economic reasons is in the range 300-800 kV.

Commercial accelerators presently preclude dose rates above about 100 kGy/sec due to limitations in practical current density. Still it should be reminded that the dose rate also increases with decreasing electron energy and hence along the electron path through the irradiated medium. High dose rates therefore can always be expected in a region where the electron energy has decayed to a few percent of its initial value. The design of irradiation chambers, of course, should not exceed the electron range and hence these dose rate effects become indistinguishable from wall effects.

4.4. A simplified reaction scheme

It is now possible to derive a simple overview on the kinetics of the EBDS process. According to the above discussion, positive ions are the most important irradiation products. They support NO_x oxidation both directly and via radical formation. SO_2 oxidation is initiated only by OH radicals:



However, radical reactions do not support NO_x oxidation straightforward. There also exist two types of reduction reactions:

(i) those yielding molecular nitrogen and N_2O as stable products; they complement oxidative NO_x removal, but do not support particle formation;

(ii) those reducing intermediate NO_2 back to NO; they counteract oxidative NO_x removal.

The latter mechanism is due to oxygen atoms which effectively reduce NO_2 (reaction 14). In consequence, any input NO molecule is trapped in the oxidation-reduction cycle between NO and NO_2, before it ends up in HNO_3, N_2 or N_2O. This corresponds to an inefficient utilization of the available radical source and also of the input energy: NO_x removal therefore becomes a nonlinear function of dose and eventually attains a saturation with increasing dose.

5. The chemistry of ammonia

A common measure of the amount of ammonia added to the waste gas is the stoichiometry ratio, defined by

$$s = \frac{[NH_3]}{[NO_x] + 2 \cdot [SO_2]}$$

For the typical s values between 0.5 and 1, the ammonia concentration is comparable or higher than those of NO_x or SO_2. Ammonia can be added at different stages of the process: Upstream, in or downstream of the irradiation chamber; a mixture of these possibilities is also of interest. The experiments have shown that ammonia should be added to the waste gas before irradiation (Baumann et al., 1987; Frank, 1988), this giving best results for both NO_x and SO_2 removal. This finding and the almost linear correlation between N_2O formation and stoichiometry ratio clearly show that ammonia does not only act as to neutralize the acids, but also takes an important part in the gas phase chemistry. In this way, ammonia provides a connecting link between the gas phase chemistry and the particle formation in the EBDS process.

5.1. Ammonia and radicals

The radical chemistry of ammonia is rather complicated and has thoroughly been investigated and discussed during recent years (e.g. Dean et al., 1982; Miller et al., 1983; Lesclaux, 1984; Dransfeld et al., 1984; Cohen, 1987). Also, the modeling approaches forwarded by Miller et al. (1983) and Cohen (1987) are found to disagree somewhat. The author has made an effort to put things together and part of this is described below.

The reactions of ammonia with H and O atoms

$$NH_3 + H \rightarrow NH_2 + H_2 \tag{19a}$$

$$NH_3 + O \rightarrow NH_2 + OH \tag{19b}$$

proceed fairly slowly under EBDS conditions; k_{19a} has been measured by Hack et al. (1986):$k_{19a} = 9.1 \cdot 10^{-15} \cdot T^{1.3} \cdot \exp(-6570/T)$ cm^3/sec and k_{19b} has been reviewed and proposed by Cohen (1987): $k_{19b} = 1.83 \cdot 10^{-18} \cdot T^{2.1} \cdot \exp(-2620/T)$ cm^3/sec. The major attack on NH_3 is by OH:

$$NH_3 + OH \rightarrow NH_2 + H_2O \tag{20}$$

Cohen (1987) uses $k_{20} = 8.32 \cdot 10^{-17} \cdot T^{1.6} \cdot \exp(-480/T)$ cm³/sec which for T = 300 ... 500 K is in good agreement with the measurements by Jeffries et al. (1986) and previous data (Miller et al., 1983; Levine, 1985).

Ammonia has also been reported to promote the recombination of HO_2 (Lii et al., 1980), but this appears negligible in the concentration regime discussed here.

The chemistry of the moderately reactive amidogen radical (NH_2), produced by reaction (20) mainly, is fairly complex and only the most obvious reaction paths are considered here. The most prominent characteristic of NH_2 is its instability against oxidation, or, vice versa, its reducing property. Thus it readily reduces NO and NO_2:

$$NH_2 + NO_2 \rightarrow N_2O + H_2O \qquad k_{21} = 2.2 \cdot 10^{-12} \cdot \exp(+650/T)\ \mathrm{cm^3/sec}$$

(DeMore et al., 1985). This reaction is the major source of N_2O in the EBDS process and accounts for the final N_2O concentration to be roughly proportional to the dose and to the stoichiometry ratio (Baumann et al., 1987).

The NH_2 + NO reaction is a key step in the thermal $DeNO_x$ process. Vibrationally excited H_2O and ground state OH radicals have been identified among the reaction products (Dreier et al., 1984 and references therein). These findings are attributed to the reaction branches

$$NH_2 + NO \rightarrow N_2 + H_2O \qquad (22a)$$

$$\rightarrow N_2H + OH \qquad (22b)$$

(Miller et al., 1983; Cohen, 1987). Reaction (22) is known to proceed faster with decreasing temperature; from the measurements by Andresen et al. (1982) and by Silver et al. (1982), the approximation

$$k_{22} = k_{22a} + k_{22b} = 1.15 \cdot 10^{-7} \cdot T^{-1.54}\ \mathrm{cm^3/sec}$$

can be derived for T = 300 ... 1000 K. This expression, taken from Cohen (1987), compares well to that used by Miller et al. (1983). The OH-formation by reaction (22) presumably increases with temperature, which may be interpreted in terms of a temperature-dependent branching ratio, $k_{22a}/k_{22b} = f(T)$, although this is not a necessary conclusion (Dreier et al., 1984; Harrison et al., 1987). It seems to be well established that $k_{22a} : k_{22b} \approx 0.83 : 0.17$ around room temperature (Dolson, 1986; Hall et al., 1986; Silver et al., 1987). Around 1000 K, $k_{22a} : k_{22b} \approx 1:1$ appears plausible (Kimball-Linne et al., 1986). In combination with the above k_{22}, these branching ratios can be interpreted by the following rate expressions, the first of which is close to earlier data reported by Hack et al. (1979):

$$k_{22a} = 1 \cdot 10^{-6} \cdot T^{-1.96} \text{ cm}^3/\text{sec}$$

$$k_{22b} = 1 \cdot 10^{-12} \cdot \exp(+330/T) \text{ cm}^3/\text{sec}$$

which the author believes to be a preliminary, but feasible assumption at T = 300 ... 1000 K. Fig. 1 gives a short overview on the literature data quoted above and compares them to the present proposal.

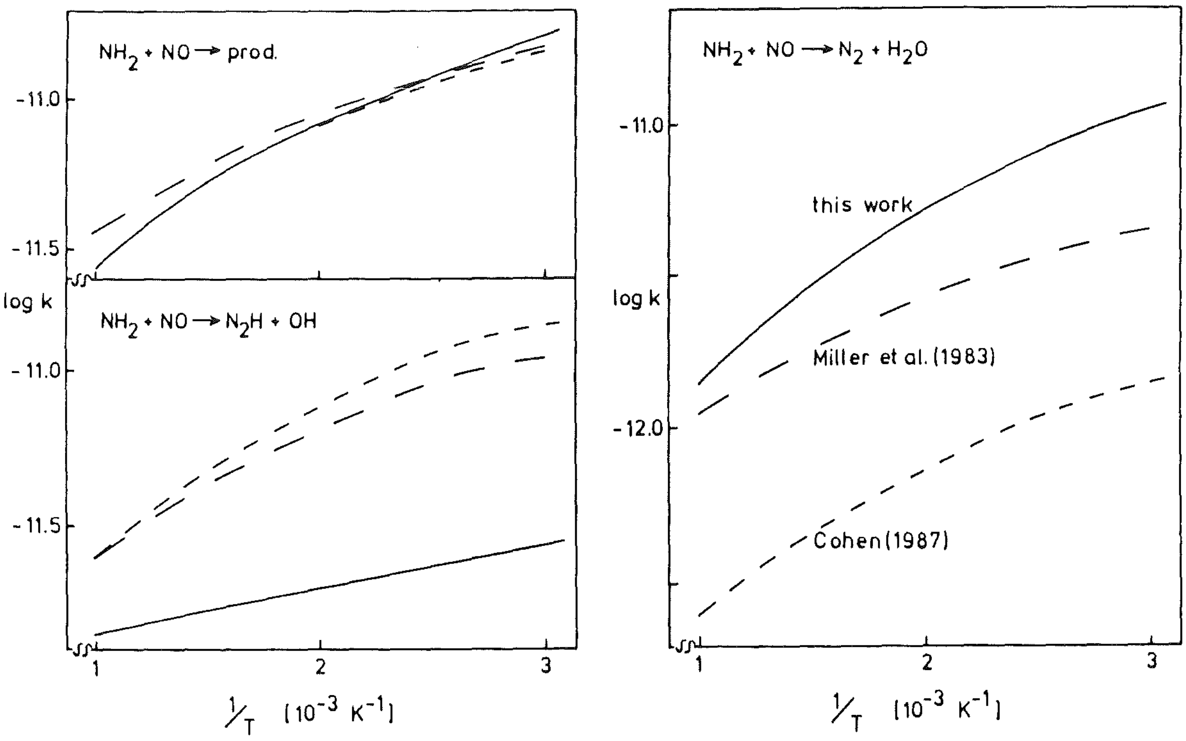


Fig. 1: Comparison of literature data on the rate constants of the reaction $NH_2 + NO \rightarrow$ prod. and of the reaction branches (22.a) and (22.b) used in this work.

The reactions (21) and (22) have been discussed here to some detail, because they represent the most important NH_2 sinks in the system under consideration and provide the key to the understanding of NO_x removal by ammonia: Since NH_2 does not react significantly with the major components of the waste gas or with SO_2 (Lesclaux, 1984), it directly supports NO_x removal. In addition, this also holds for the side reaction

$$NH_2 + O \rightarrow HNO + H \qquad k_{23a} = 1.1 \cdot 10^{-9} \cdot T^{-0.5} \text{ cm}^3/\text{sec}$$

$$\rightarrow NH + OH \qquad k_{23b} = 1.2 \cdot 10^{-11} \text{ cm}^3/\text{sec}$$

(Dransfeld et al., 1984; Miller et al., 1983). Like reaction (21), the reaction (23) opposes the undesired $NO_2 + O$ reaction discussed in sect. 4.3. Further, reaction

(23) supports the oxidative pathway through regeneration of OH via reaction (23.b) and indirectly, since reaction (23.a) is followed by

$$HNO + O_2 \rightarrow NO + HO_2 \qquad (17)$$

$$\rightarrow NO_2 + OH \qquad (18)$$

and by

$$H + O_2 + M \rightarrow HO_2 + M$$

Especially because of its potential ability to counteract the oxidation-reduction cycle between NO and NO_2, reaction (23) is thought to be the sole radical-radical reaction of importance in the EBDS-process (Mätzing, 1989). In this context it is worth noting that the above reaction sequence may not only be interpreted in terms of NO_x reduction, but also from the viewpoint of NH_3 oxidation.

Besides the above discussed favourable role of NH_2 in the EBDS process, it must not be forgotten that its formation mainly proceeds by consumption of OH: $NH_3 + OH \rightarrow NH_2 + H_2O$ (20). Since the bimolecular reaction (20) proceeds with a net rate comparable to that of the termolecular SO_2 + OH reaction, the model calculation predicts a slight decrease of the radiation induced sulfate formation with increasing NH_3-stoichiometry ratio (Mätzing, 1987a). This seems to be a subtle contradiction to experimental results which show a substantial increase of sulfate formation with rising ammonia concentration (Paur et al., 1988 a). On the other hand, it does not appear feasible to interpret the measured sulfate concentrations in terms of genuine radiation chemical effects (Frank, 1988; Jordan, 1988): Rather, there is much evidence for additional purely thermal and/or heterogeneous sulfate formation steps which are not easy to isolate from radiation induced reactions experimentally. These will be discussed below.

5.2. The formation of ammonium salts

Two stable acids are formed by the gas phase chemistry of the EBDS process, as described above: HNO_3 and H_2SO_4. They have different physical properties and those of interest here are their vapour pressures which differ by many orders of magnitude. The vapour pressure of sulfuric acid, in particular, is so small at T = 273 ... 373 K (Roedel, 1979; Perry et al., 1984) that the existence of gaseous sulfuric acid even becomes questionable in this temperature range. It is therefore reasonable to assume that sulfuric acid nucleates prior to reaction with ammonia. Ammonium sulfate formation thus is probably not a gas-solid transition, but rather a heterogeneous reaction determined by the rate of incorporation of ammonia into sulfuric acid droplets. When both the nucleation of sulfuric acid and the transport of ammonia to the surface of the nucleating droplets are assumed to be fast processes, it appears a good approximation to substitute the real process by the fast dummy reactions

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$$

$$NH_3 + NH_4HSO_4 \rightarrow (NH_4)_2SO_4$$

(Rolle et al., 1984; Person et al., 1985). Another argument for this abbreviated reaction modeling is the thermal stability of ammonium sulfate, which decomposes only above about 150 °C.

This treatment results in the prediction that H_2SO_4 be converted to $(NH_4)_2SO_4$ completely in the presence of sufficient ammonia. The chemical composition of the EBDS-aerosol, however, shows something different: While in case of low relative humidity, the chemical composition indeed corresponds to a mixture of NH_4NO_3 and $(NH_4)_2SO_4$ (Paur et al., 1988 b), some NH_4^+-deficiency shows up in case of high relative humidity (Paur et al., 1988 d). The NH_4^+-deficiency can be interpreted such that at high relative humidity the NH_3-H_2SO_4 reaction is not complete at the time scale available, i.e. at the point of aerosol sampling. The formation of $(NH_4)_2SO_4$ is complete at later stages, perhaps only in the product filter under some conditions. The heterogeneous reaction between sulfuric acid droplets and gaseous ammonia can be modeled according to the concept described in chapter 6.

Unlike sulfuric acid, nitric acid cannot be expected to nucleate under typical EBDS conditions and this view is strongly supported by the observation that in the absence of ammonia, no nitrate can be detected in the aerosol (Paur et al., 1988 a). Note that this experimental fact also is an argument against ion-assisted nucleation of nitric acid. Therefore, it appears probable that ammonium sulfate and nitrate formation are independent processes which are determined only by the difference of their vapour pressures. A mixed, both nitrate and sulfate containing aerosol can thus only result from the coagulation of the two chemically different and independently developing aerosols. The condensation of NH_4NO_3 at the surface of incompletely neutralized H_2SO_4 droplets cannot definitely be excluded, but may be speculated to invoke the decomposition

$$NH_4NO_3 \xrightarrow{H_2SO_4} N_2O + 2\,H_2O$$

In comparison with ammonium sulfate, the ammonium nitrate has a much higher vapour pressure or, equivalently, a much lower thermal stability which is determined by the heterogeneous equilibrium

$$NH_4NO_3\,(s) \rightleftharpoons NH_3\,(g) + HNO_3\,(g)$$

It is not easy to extract a conclusive equilibrium constant for this process from the literature, because this equilibrium is not a unique function of temperature, but also a function of the ambient water vapour pressure (relative humidity), since ammonium nitrate is a hygroscopic substance (Stelson et al., 1982). Eq. (4) given by Stelson et al. (1982) can be interpreted to imply an average free energy of sublimation of dry NH_4NO_3 around 86.65 kJ/mol over the temperature range 293 ... 400 K. On the other hand, Heicklen et al. (1975) found

$$[NH_3] \cdot [HNO_3] = 5.8 \cdot 10^{27}\ \text{molec}^2 / \text{cm}^6 \approx 10\ \text{ppm}^2$$

as the necessary condition for the onset of NH_4NO_3 nucleation at $T = 298$ K. If this value is interpreted in terms of thermodynamic equilibrium, $\Delta G^\circ = 62.79$ kJ/mol is obtained which is markedly smaller than that by Stelson et al. (1982). Unfortunately, the data by Heicklen et al. (1975) hold at $T = 298$ K only. Due to lack of further information, the "free enthalpy" derived from their data is considered independent of temperature tentatively. With this restriction one arrives at the equilibrium vapour pressures of NH_4NO_3 in Table I. They differ by about two and three orders of magnitude at $T = 298$ K and $T = 370$ K, resp. A priori, this difference is not a contradiction, since according to the different approaches, which they are derived from, they have different meanings: The kinetic study by Heicklen et al. (1975) refers to the maximum possible concentrations of gaseous NH_3 and HNO_3 prior to nucleation, while the thermodynamic study by Stelson et al. (1982) gives the corresponding minimum concentration which can be expected in the gas phase above the (flat) surface of particulate NH_4NO_3.

The above discussion can be summarized as to interpret the apparent difference of the two data sets in terms of a supersaturation ratio S. S is given by

$$S = \exp\,(+\ 2850/T)$$

using the assumptions above. Interestingly, a decrease of supersaturation ratio with rising temperature is obtained here for a gas-solid transition with chemical reaction. If this is true, the reaction

$$NH_3 + HNO_3 \rightarrow \text{solid } NH_4NO_3$$

Table I: Estimated equilibrium vapour pressures above dry NH_4NO_3

ΔG° [kJ/mol]	86.65 (Stelson et al., 1982) $p_{NH_3} = p_{HNO_3}$		62.79 (Heicklen et al., 1975) $p_{NH_3} = p_{HNO_3}$	
	[atm]	[ppb]	[atm]	[ppb]
T = 298 K	$2.9 \cdot 10^{-8}$	29	$3.4 \cdot 10^{-6}$	3400
T = 370 K	$8.4 \cdot 10^{-7}$	840	$4 \cdot 10^{-5}$	40 000

would have to have a higher activation energy than the reverse evaporation reaction. Certainly, more experimental data are needed on this interesting topic, since the above discussion is based on only one kinetic measurement at T = 298 K and this also means that the above derived temperature dependence of S should be regarded rather as a question than as conclusive result.

The nucleation rate of NH_4NO_3 has been evaluated by Heicklen et al. (1975) in terms of an apparent 8th order process:

$$\frac{d[NH_4NO_3]}{dt} = (1.26 \cdot 10^{-28} \cdot [NH_3] \cdot [HNO_3])^8 \; cm^{-3} \cdot min^{-1}$$

and the second order condensation rate constant is given by the same authors to be $2 \cdot 10^{-8}$ cm^3/sec at T = 298 K. These rates compare to those of the very fast ion recombination rates (sect. 3.4). Their energies of activation would have to be as high as 25 kJ/mol in order to decrease them to the maximum possible for bimolecular reactions of neutrals. Applied to EBDS conditions, this infers nitric acid formation to be the rate-determining step for NH_4NO_3 formation, which is plausible. The author has found this concept useful to model the particulate nitrate concentrations established by EBDS processing.

It remains to be noted that the low equilibrium vapour pressures over dry NH_4NO_3 (Stelson et al., 1982) already correspond to an almost complete consumption of gaseous substrate. With increase of the relative humidity in the gas phase, these equilibrium vapour pressures must be expected to decrease (Stelson et al., 1982). This means that only ppb-amounts of substrate could be converted to NH_4NO_3 on account of increasing relative humidity, which is beyond the scope of measurable mass concentrations. Therefore, the experimentally established increase of nitrate formation with increasing relative humidity (Paur et al., 1988 a) is not due to a simple shift of the thermodynamic equilibrium: Nitric acid formation is enhanced by increasing relative humidity via the radiation induced ionic pathway mentioned in sect. 4.2:

$$NO_2^+(H_2O)_2 + H_2O \rightarrow HNO_3 + H_3O^+(H_2O)$$

This pathway has recently been found adequate to model the dependence of nitrate mass concentration on relative humidity (Mätzing, 1987 a).

5.3. Ammonia and sulfur dioxide

The direct interaction of gaseous ammonia and sulfur dioxide is known to yield ammonium sulfate under atmospheric conditions, i.e. at comparatively low temperatures in the presence of oxygen and water vapour. In the context of atmospheric pollutants, this SO_2/NH_3-reaction is fairly well understood and is known to occur at a time scale of hours (Friedlander, 1977; Levine, 1985; Seinfeld, 1986). In the range of waste gas conditions, on the contrary, fairly little is known on the reaction between gaseous ammonia and sulfur dioxide, although corresponding experiments have been conducted and proposed (eg. Hartley et al. (1975); Landreth et al. (1975) and references therein). From these and similar studies it is known that a solid product can form from a mixture of gaseous ammonia, sulfur dioxide and water in the temperature range T = 290 ... 320 K. The solid product has no uniform composition, but consists of a mixture of ammonium salts like sulfite, sulfate, pyrosulfite and others. The N/S ratio of the solid and its water content depend in a rather complex way on the initial gas phase composition and on temperature. Landreth et al. (1975) derived an equilibrium constant

$$\ln K_p\,[\mathrm{atm}^{-4}] \approx -56.5 + 26500/T\,[K]$$

for the gas-solid equilibrium

$$2\,NH_3 + SO_2 + H_2O \rightleftharpoons (NH_3)_2\,SO_3$$

Their derivation is based on vapour pressure measurements and the authors have identified ammonium sulfite to be the <u>major</u> reaction product (Landreth et al., 1975). The above equilibrium must be regarded as an approximation for two reasons:

(i) there are still doubts concerning the effective stoichiometry of the reaction;

(ii) the above equilibrium suggests a quatermolecular reaction which is very unlikely to occur in the gas phase as such, a kinetic description would certainly involve a mechanism of two or more steps.

The study by Hartley et al. (1975) gives some hints on the kinetics of the ammonia-sulfur dioxide reaction. From a re-evaluation of the data, the author has found the following rate law for the formation of the solid product:

$$\frac{dc}{dt} = k \cdot \ (c_{max} - c)$$

in which c and c_{max} are the intermediate and final product concentrations resp., k is the apparent first order rate constant (see Fig. 2). A rate law of this kind is well known from other studies of nucleation and condensation phenomena (Elias, 1981; Stumm et al., 1981). A number of experiments described by Hartley et al. (1975) have been evaluated in this way and k was found to be in the range 7... 17 sec^{-1}. The tentative plot in Fig. 3 may indicate a dependence of k on the stoichiometry ratio, but care must be taken not to over-interpret the data.

These examples may suffice to point out the complexity of ammonia-sulfur dioxide interaction. The problem becomes even worse, when temperatures of the order of 350 K apply, i.e. under EBDS conditions, because this is above or amidst the thermal decomposition range of simple ammonium sulfites.

From many EBDS research studies it is well known that ammonia and sulfur dioxide are degraded solely upon mixing, i.e. in the absence of electron beam irradiation. From these studies, it could be established that the so-called "thermal" NH_3-SO_2 reaction

(i) is favoured by high ammonia concentration,

(ii) is favoured by high relative humidity,

(iii) does not form an aerosol-like particulate

(e.g. Baumann et al., 1987; Paur et al., 1988a; Frank et al., 1988; Wittig et al., 1988 b). Recent investigations preclude the thermal NH_3-SO_2 reaction to be an artefact invoked by the measuring technique or to generate a sub-micron aerosol which escapes the filter (Paur et al., 1988 b; Paur, 1988 c). Up to date, there exists no conclusive idea on the nature of this thermal NH_3-SO_2-reaction.

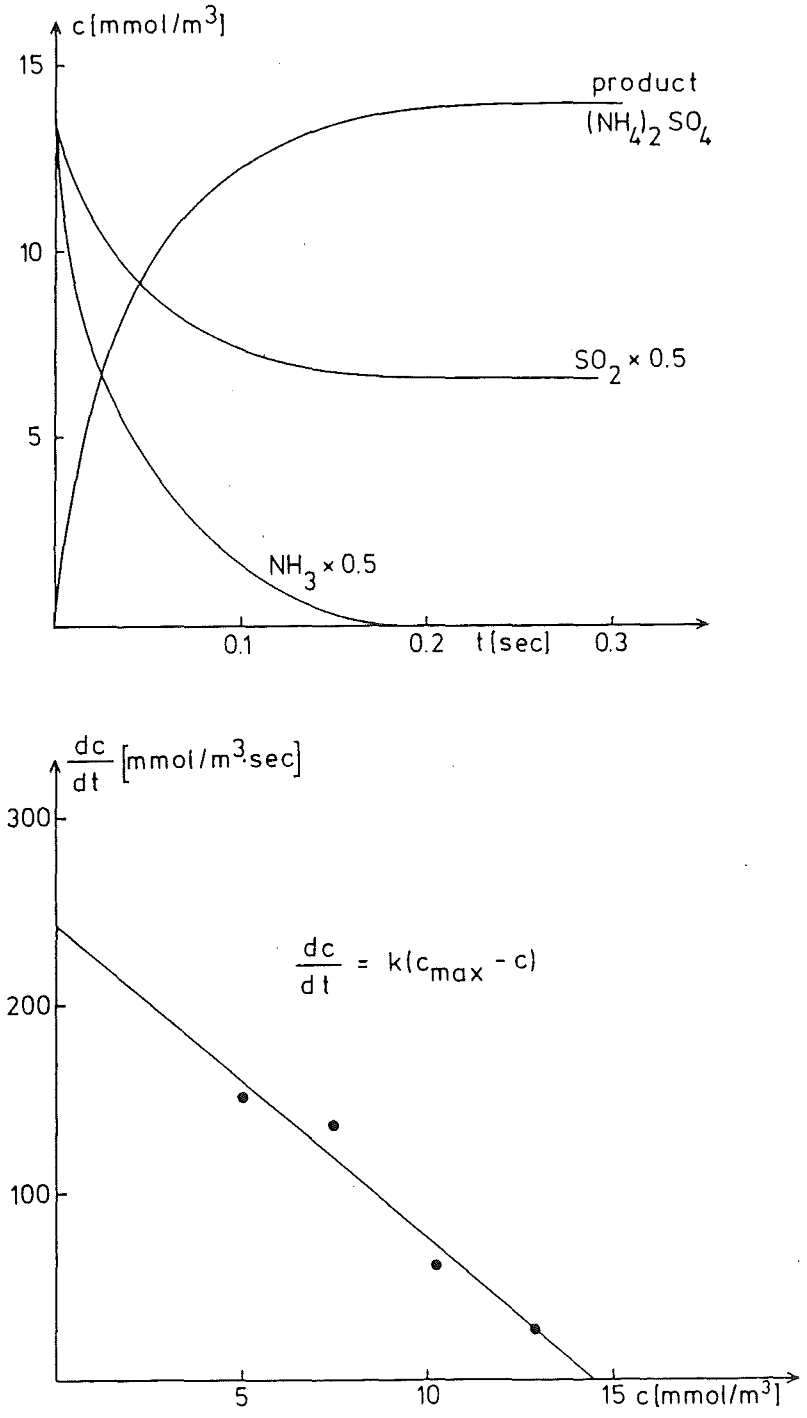


Fig. 2: Plots of measured concentrations vs. time and determination of rate constant k for product formation in experiment series D from Hartley et al. (1975)

A first, tentative proposal has recently been published by Jordan (1988) and Jordan et al. (1988). It involves the formation of a gaseous adduct (charge-transfer complex) from the Lewis base NH_3 and the Lewis acid SO_2. This gaseous complex is thought to form ammonium sulfate upon irradiation. Such a Lewis

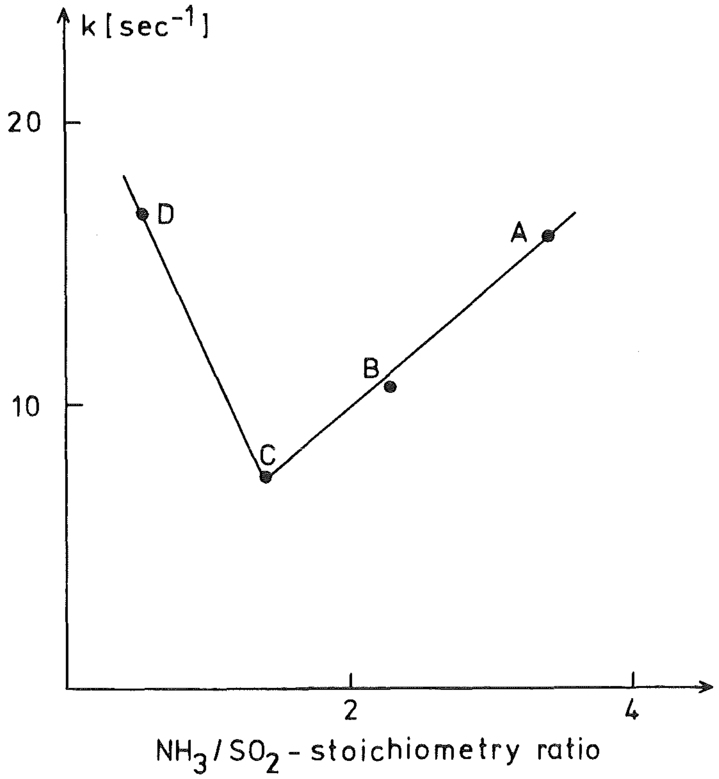


Fig.3: Rate constant for product formation as function of ammonia-stoichiometry, evaluated for experiment series A, B,C,D reported by Hartley et al. (1975)

acid-base reaction between NH_3 and SO_2 has been studied by Landreth et al. (1974) under unhydrous conditions. In the temperature range T = 278 ... 318 K, these authors even observed particle formation from dry NH_3 and SO_2 and give a reaction enthalpy $\Delta H = 40$ kJ/mol for the process

$$NH_3 \cdot SO_{2(s)} \rightleftharpoons NH_3 + SO_2$$

This ΔH-value is in excellent agreement with the calculated energy for the N-S bond in that complex (Lucchese et al., 1976; Douglas et al., 1978). A kinetic study of this subject would certainly be of interest both from the modeling and application point of view.

5.4. Effects of ammonia addition

In the radiation induced gas phase chemistry of the EBDS process, the OH radical has been shown to play the key part for nitric and sulfuric acid formation; NO, NO_2 and SO_2 compete for OH. The added ammonia enters into this competition: About 5% of the ammonia (i.e. roughly 50 ppm usually) react with OH. Thereby, the NH_2 radical is formed which reduces NO and NO_2 to yield molecular nitrogen and N_2O as stable gaseous products. The amounts of N_2 and N_2O formed in this way are approximately equal and are around 1-2 ppm/kGy typically. Up to a dose around 10 kGy, this is the only significant N_2O source in the EBDS process. As molecular nitrogen source, this mechanism is about half as effective as the NO + N reaction (sect. 4.3) and readily increases the total nitrogen formation to about 10-15% of the input NO.

The major part of the ammonia remains available for ammonium salt formation. As the parent acids differ remarkably in their vapour pressures, the particulate formation is likely to involve different mechanisms:

(i) ammonium nitrate is formed from gaseous nitric acid and ammonia directly;

(ii) ammonium sulfate is formed from a heterogeneous reaction between gaseous ammonia and nucleating sulfuric acid droplets.

High relative humidity has been reported to increase the aerosol mass. For ammonium nitrate, this can be explained by a corresponding increase of nitric acid formation. In the literature, only limited data are available on the direct interaction of ammonia and sulfur dioxide which in EBDS studies has been found to be of "thermal", i.e. not radiation induced, origin.

6. Heterogeneous chemistry

In the preceding chapters, the kinetics of the EBDS process have been discussed in terms of homogeneous gas phase reactions yielding gaseous and solid products. The importance of heterogeneous processes which occur at the surface of the evolving aerosol has implicitly been mentioned in the context of ammonium nitrate formation (sect. 5.2). This importance of heterogeneous chemical reactions is emphasized by experimental findings which state

(i) particulate formation to depend on the relative humidity

(ii) removal yields to be increased by filtration

(Paur et al., 1988a, b; Frank et al., 1988). Another hint to this point comes from the theoretical treatment: According to models on the pure gas-phase chemistry of the EBDS process, nitrous acid would be a major product species due to its unexpected kinetic stability discussed in sects. 4.1 and 4.2. This is further demonstrated in the results by Busi et al. (1988) and Person et al. (1988). Contrary to its kinetic stability in the gas phase, HNO_2 is highly unstable against heterogeneous decomposition, a process which also depends on the kind of surface involved (Kaiser et al., 1977a). Altogether, the high HNO_2-concentrations predicted by gas phase chemical EBDS models should either be detectable as particulate NO_2^- or be destroyed at the particulate surface. Since definitely no NO_2^- is found in the particulate samples (Jordan et al., 1986; Paur et al., 1986; Paur, 1988c), the heterogeneous decomposition of HNO_2 must play a crucial part of the NO_x-chemistry in the EBDS process.

In the context of EBDS processing, the term "heterogeneous chemistry" has most often been used in a way as to summarize those experimental findings which are not readily understood by genuine gas phase reactions. Recently, Busi et al. (1988) have emphasized the need for a more precise terminology. Reactions associated with the filtration process, for instance, would probably be a mixture of reactions occurring at gas-solid and gas-liquid interfaces as well as pure liquid-phase reactions. Trace gas removal across the filtration unit is easy to measure compared to processes involving particulate dispersions in the gas phase. Only the latter are addressed here in view of their relation to the gas composition and particulate mass loading transferred to the filter. In order to get an idea about the particle reactivity, one likes to have a reliable estimate at least on the physical properties (surface) of the aerosol arising from electron beam irradiation of waste gas. Such an estimate has often been ignored in previous publications and it will be the first subject of the subsequent discussion.

6.1. The aerosol surface

The specific surface A_s of an aerosol consisting of spherical particles with diameter d is given by

$$A_s = \frac{1.5}{\rho \cdot d}$$

where ρ is the particulate density. The effective surface of that aerosol, A_e [m^2/m^3], is A_s times the mass concentration c [g / m^3]. Therefore, $A_e \sim c/d$ is determined by the rate of particulate mass formation and particle growth in a kind of an antagonistic way:

(i) nucleation increases c

(ii) condensation increases both c and d

(iii) coagulation increases d.

The isolated effect of coagulation on particle size can be estimated from the well known theory of coagulation of monodisperse hard spheres (Friedlander, 1977; Hidy et al., 1970). This has been done for typical mass concentrations and particle diameters in the range d = 0.01 - 1 µm. Under EBDS conditions, this size range spans the whole transition regime between continuous and molecular flow conditions; in the transition regime, the coagulation rate must be expected to be up to a factor of about 5 higher than in the free molecule regime (Hidy et al., 1970). As for a rough estimate, the author has adopted the free molecule approximation to calculate the coagulation rate over the size range mentioned. Table II gives the characteristic time scales τ_K at which the particle number density reduces to 1/e. The estimate states that particle coagulation cannot yield particles with diameters much larger than about 0.1 µm, since this would require coagulation times much longer than a second, i.e. a much longer time than available under EBDS conditions. For a particulate density around 1.5 g/cm^3 this gives a specific surface $A_s > 10$ m^2/g of the nucleating aerosol. This result is in excellent

Table II: Coagulation time scales (T = 343 K, ρ = 1.5 g/cm^3)

c [mg/Nm^3]	200	1000	200	1000	200	1000
d [µm]	0.01	0.01	0.1	0.1	1	1
τ_K [sec]	0.01	0.002	3	0.7	1000	200

agreement with a rigorous treatment of the nucleation and growth of sulfuric acid droplets under EBDS conditions (Paur et al., 1988 b; Bunz, 1988). According to this study, A_s is 30 m^2/g at the incidence of H_2SO_4 nucleation and decreases to 5 m^2/g within less than 2 sec (Fig. 4).

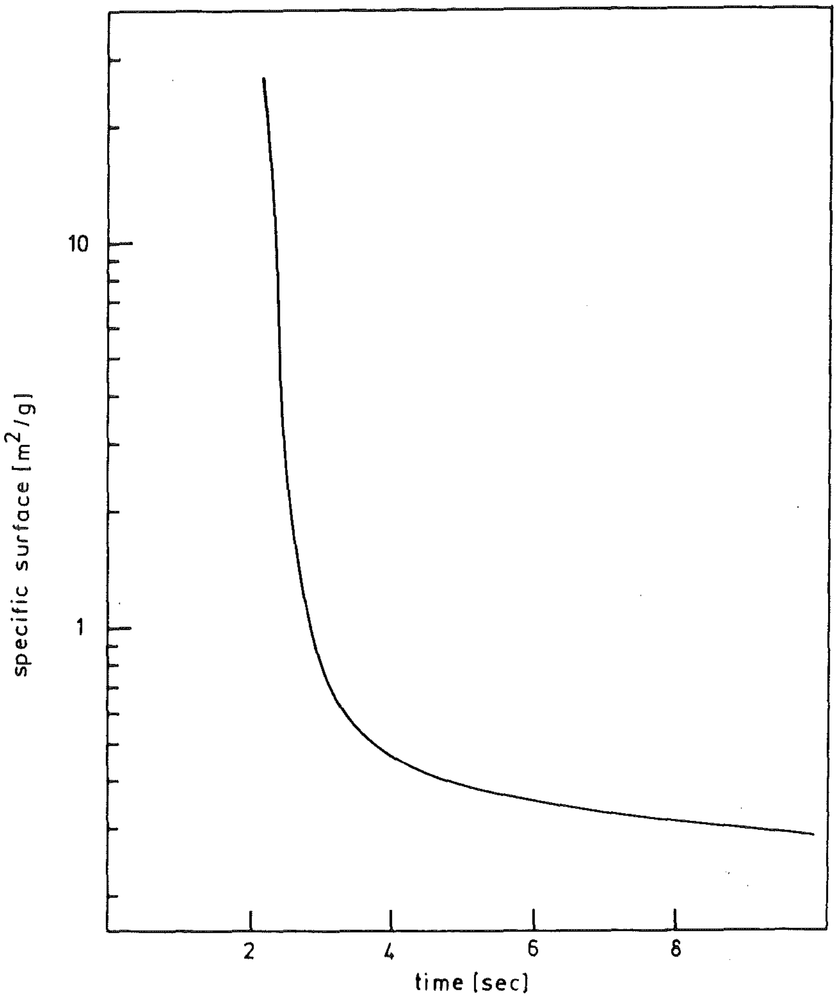


Fig. 4: Specific surface of nucleating H_2SO_4 droplets under EBDS conditions

These theoretical considerations are in good agreement with experimental size determinations of the ammonium salt particulate (Jordan et al., 1986) and permit an estimate of the rate constant for gas to particle transfer, k_{het}. From the free molecule theory, a lower limit

$$k_{het} = 0.25 \cdot \alpha \cdot \bar{v} \cdot A_e$$

is given (Hidy et al., 1970), in which $\bar{v}$ is the mean thermal velocity of the gas molecule and α is a dimensionless factor between 0 and 1 which gives a measure of the reaction probability. For $\bar{v} \approx 400$ m/sec and $A_e \approx 5$ m^2/m^3, this gives $k_{het} \approx$

500 sec^{-1}, if α is 1. This corresponds to a first order halflife time around 1 msec. Note, of course, that gas-particle reactions need not be transport limited.

6.2. Heterogeneous reactions

When introducing heterogeneous reactions into a chemical kinetics code, the problem of the stoichiometry of these reactions must be dealt with: As no detailed kinetic studies on single heterogeneous gas-solid reactions at the surface of airborne particles exist, these must either be handled with plausible assumptions or only the loss of reactants can be calculated assuming the reaction products to be unimportant or inert.

The latter approach has been forwarded in a study on the effect of heterogeneous ion sinks in the EBDS process (Mätzing et al., 1987b). The effect has been found to be negligible which simply reflects the fact that ion-particle transfer proceeds much slower (sect. 6.1) than ion-molecule reactions (sect. 3.4).

The above simple approach is no longer feasible, if one considers the heterogeneous HNO_2 decomposition mentioned earlier: In this case, assumptions about the reaction products have to be made. Busi et al. (1988) have proposed that nitrous acid enters into the particulate phase and becomes mainly reduced to N_2O:

$$2\ HNO_2 + 2\ SO_2 \cdot H_2O \rightarrow 2\ HSO_4^- + N_2O + H_2O + 2\ H^+$$

To the author's opinion, this reaction should be negligibly slow, because HNO_2 in solution is likely to decompose upon warm-up and can be reduced effectively to N_2O by strongly reducing reactants like sodium amalgam only (Holleman-Wiberg, 1976). Recent environmental studies have shown that the aqueous phase oxidation of SO_2 by HNO_2 and other atmospheric constituents proceeds at time scales above half an hour (Chang et al., 1981; Seinfeld, 1986). Further, the quantitative transformation of the calculated intermediate HNO_2 to N_2O would yield N_2O levels in the 50 ppm range at D = 10 kGy (Busi et al., 1988) which appears too high (Baumann et al., 1987).

The author has found the following decomposition reactions very promising:

$$\begin{aligned} HNO_2 &\rightarrow 1/3\ HNO_3 + 2/3\ NO + 1/3\ H_2O \\ &\rightarrow 0.5\ NO_2 + 0.5\ NO + 0.5\ H_2O \end{aligned}$$

using α values in the range 0.1 ... 0.01. These reactions are known from aqueous phase chemistry (Holleman-Wiberg, 1976). Another promising approach seems to be the heterogeneous oxidation of SO_2 by HNO_3:

$2\,HNO_3 + SO_2 \rightarrow 2\,NO + H_2SO_4 + O_2$

These reactions have been found useful to explain the saturation of NO_x removal with increasing dose (Jordan, 1988). Yet, all models of heterogeneous reactions, both at the aerosol surface and at the filter, suffer from the present lack of direct experimental verification and therefore, model approaches can only be based on plausibility assumptions on the kind of reactions and adjustments of appropriate reaction probabilities.

7. Summary

Detailed theoretical and model results of the EBDS process have lead to a profound understanding of its physical and chemical fundamentals. The following results are directly related to industrial application:

- (i) dose rate does not affect removal efficiencies,
- (ii) the measured NO_x removal results from both oxidative and reductive reaction pathways,
- (iii) multistep irradiation is most effective upon intermittent NO_2 removal,
- (iv) the EBDS process works most efficiently in case of simultaneous NO_x and SO_2 removal,
- (v) ammonia promotes both NO_x removal and particulate formation,
- (vi) relative humidity crucially affects removal efficiencies,
- (vii) the resulting aerosol must be expected to consist of particles in the sub - µm size range.

For theoretical and practical purposes more detailed informations are desirable on the following subjects:

- (i) measurements of intermediate HNO_2 concentrations,
- (ii) NH_2 formation and consumption,
- (iii) thermal NH_3/SO_2 reaction
- (iv) heterogeneous gas-particle reactions.

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Part II

The AGATE - Code

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1. Introduction

Part II of this report gives a complete listing of the AGATE code, which has been developed for a quantitative description and investigation of the chemical kinetics pertaining to the EBDS process. The code is continuously being updated, e.g. concerning new data on temperature-dependent reactions or specific mechanisms. The present listing gives the code status in spring 1988.

2. The structure of the AGATE-Code

Input values to the AGATE-Code are: waste gas composition in concentrations by volume, temperature, pressure, the irradiation dose D_0 in J/g units and a parameter σ [sec] which determines the width of the Gaussian dose rate profile:

$$\dot{D} = \frac{D_0}{\sigma \cdot \sqrt{2\pi}} \cdot exp[-\frac{1}{2}(\frac{t-\tau}{\sigma})^2]$$

From the input data, τ is calculated by giving $\dot{D}$ a small positive start value at $t = 0$. The second time derivative of the dose, $\ddot{D} = \dot{D} \cdot (\tau - t) / \sigma^2$, is used to calculate the actual dose rate at time t by integration. The active species concentrations are calculated from

$$\frac{dn}{dt} = G_n \cdot \dot{D} \cdot x_i \cdot \rho$$

where G_n is the G-value for species n obtained by irradiation of component i with mole fraction x_i. ρ is the average gas density under input conditions. By choosing G_n [molecules / 100 eV], $\dot{D}$ [100 eV / g · sec] and ρ [g / cm^3], dn/dt results in [cm^{-3} · sec^{-1}]. The G-values are listed in Table I.

The reactions initiated by active species generation are listed in Tables II - VIII. The net reaction rates for each reaction (or irradiation step) are calculated between successive integration steps from the stored rate constants and the actual reactant concentrations. These net rates are used to calculate the time derivative of each single species according to the stoichiometry of each reaction. The integration is performed with a commercial subroutine (Subroutine Library Specification, Harwell 1979) which employs a Gear algorithm for the integration of stiff ordinary differential equations. The computational accuracy, based on atomic mass balance, is 10^{-11} % or better.

3. Data representation

The data representation in Tables I - VIII is in principle self-explaining and various notes are included in the tables. Some additional remarks are summarized below.

Table I. The irradiation G-values are tabulated according to a convenience widely used in the literature. For inclusion into the numerical calculation, these steps have been converted to stoichiometric equations. The electrons supplied by the accelerator do not appear explicitly in the code. Those electrons which originate from ionization processes are arbitrarily termed "hot electrons" in the tabulation. They are allowed to thermalize before entering into reactive steps (Table III). This means that all thermal electrons are treated as having equal properties determined by the low-energy tail of the true thermal energy distribution.

Tables II - VI give the reactions implemented in the AGATE code. All rate constants are in cm^3, sec units. Some reactions (e.g. mutual ion recombination) have rate constants which are a sum of bimolecular and termolecular contributions. In this context, M denotes the overall molecule concentration [cm^{-3}]; M has been set to 99 % of the value obtained from the ideal gas law.

Where available, the temperature dependence of rate constants is included using T[K].

Some rate constants depend explicitly on the concentration of water vapour; in this case, [H_2O] is in [cm^{-3}].

Table VII compiles almost all third order reactions of neutrals. Where indicated, k_0 is used with the assumption that the low pressure limit applies. In the other cases, k_0, k_∞ and F_C are given, from which

$$k = \frac{k_1}{1 + k_1 / k_\infty} F_C^{\{1 + [(\log k_1 / k_\infty) / (0.75 - \log F_C)]^2\}^{-1}}$$

is obtained with $k_1 = k_0 \cdot [M]$. For reactions in the H_2 - O_2 - CO system, the third body efficiencies given by Warnatz (10) are used to calculate k_1:

H_2	O_2	N_2	H_2O	CO	CO_2	Ar	He
1.0	0.4	0.4	6.5	0.75	1.5	0.35	0.35

Table VIII shows some heterogeneous reactions which have been considered so far. According to chapter 6 of Part I rate constants of the form $k_{het} = 0.25 \cdot \alpha \cdot \bar{v} \cdot A_e$ [sec^{-1}] are used, where $\bar{v}$ is the thermal velocity of the gaseous species considered and A_e the effective (actual) particulate surface. In case that two different species are transfered to the particulate surface, the minimum of their different velocities is used. Table VIII gives preliminary α values. Further investigation is currently in progress.

Ammonium nitrate formation is modeled according to the 8th order expression given by Heicklen et al. (73) using

$$[HNO_3] \cdot [NH_3] \geqq M^2 \cdot \exp(-7500 / T)$$

as the necessary condition for the onset of nucleation.

Ammonium sulfate formation has so far been modeled by two fast dummy reactions forming NH_4HSO_4 and $(NH_4)_2SO_4$, respectively. A heterogeneous description of this process is under development.

Table I. Radiolytic processes

			G (molecules/100 eV)
N_2	→	N_2^*	0.29
N_2	→	$N(^2D)$	0.885
N_2	→	$N(^2P)$	0.295
N_2	→	$N(^4S)$	1.18
N_2	→	$N_2^+ + e^-$	2.27
N_2	→	$N^+ + N + e^-$	0.69
O_2	→	O_2^*	0.077
O_2	→	$O(^3P) + O(^1D)$	1.82
O_2	→	$O(^3P) + O^*$ (above ^1S level)	0.18
O_2	→	$O(^3P) + O^+ + e^-$	0.80
O_2	→	$O(^1D) + O^+ + e^-$	0.43
O_2	→	$O_2^+ + e^-$	2.07
H_2O	→	$H_2 + O$	0.45
H_2O	→	$OH + H$	3.58
H_2O	→	$H_2O^+ + e^-$	1.99
H_2O	→	$H_2^+ + O + e^-$	0.01
H_2O	→	$H^+ + OH + e^-$	0.67
H_2O	→	$OH^+ + H + e^-$	0.57
H_2O	→	$O^+ + H_2 + e^-$	0.06
CO_2	→	$CO + O$	4.51
CO_2	→	$CO_2^+ + e^-$	2.24
CO_2	→	$CO^+ + O + e^-$	0.51
CO_2	→	$C^+ + 2\,O + e^-$	0.07
CO_2	→	$O^+ + CO + e^-$	0.21

Note: O_2^* and N_2^* are treated like $O_2(^1\Delta_g)$ and $N_2(A)$ in the model. Data are from refs. (3) and (60).

Electrons arising from radiolysis are allowed to thermalize prior to reactions (see Table III).

Table II. Positive ion-neutral reactions

1	$N_2^+ + O_2 \rightarrow O_2^+ + N_2$	$k = 3.9 * 10^{-10} * exp(-T/143)$	(27)
2	$N_2^+ + O_2 \rightarrow NO^+ + NO$	$k = 1.0 * 10^{-17}$	(16)
3	$N_2^+ + H_2O \rightarrow H_2O^+ + N_2$	$k = 2.0 * 10^{-9}$	(26)
4	$N_2^+ + CO_2 \rightarrow CO_2^+ + N_2$	$k = 8.3 * 10^{-10}$	(16, 59)
5	$N_2^+ + NO \rightarrow NO^+ + N_2$	$k = 3.3 * 10^{-10}$	(26)
6	$N_2^+ + NO_2 \rightarrow NO_2^+ + N_2$	$k = 3.0 * 10^{-10}$	(16)
7	$N_2^+ + SO_2 \rightarrow SO_2^+ + N_2$	$k = 5.0 * 10^{-10}$	(26)
8	$N_2^+ + NH_3 \rightarrow NH_3^+ + N_2$	$k = 1.9 * 10^{-9}$	(26)
9	$N_2^+ + O_3 \rightarrow O_2^+ + O + N_2$	$k = 1.0 * 10^{-10}$	(16)
10	$N_2^+ + N_2O \rightarrow N_2O^+ + N_2$	$k = 3.0 * 10^{-10}$	(16)
11	$N_2^+ + H_2 \rightarrow H_2^+ + N_2$	$k = 4.0 * 10^{-10}$	(16)
12	$N_2^+ + CO \rightarrow CO^+ + N_2$	$k = 7.0 * 10^{-11}$	(26)
13	$N_2^+ + OH \rightarrow OH^+ + N_2$	$k = 4.6 * 10^{-10}$	(16, 59)
14	$N_2^+ + H \rightarrow H^+ + N_2$	$k = 2.5 * 10^{-10}$	(16, 59)
15	$N_2^+ + O \rightarrow NO^+ + N$	$k = 1.4 * 10^{-10}$	(4, 16, 78)
16	$N_2^+ + O \rightarrow NO^+ + N(^2D)$	$k = 1.8 * 10^{-10} * (300/T)$	(16, 55, 75)
17	$N_2^+ + O \rightarrow O^+ + N_2$	$k = 6.0 * 10^{-12}$	(55)
18	$N_2^+ + N \rightarrow N^+ + N_2$	$k = 1.0 * 10^{-11}$	(55)
19	$N_2^+ + N + M \rightarrow N_3^+ + M$	$k = 1.0 * 10^{-29} * (300/T)$	(16)

20	$N_2^+ + N_2 + M \rightarrow N_4^+ + M$	$k = 5.0 * 10^{-29} * (300/T)$	(16)
21	$N^+ + O_2 \rightarrow NO^+ + O$	$k = 2.6 * 10^{-10}$	(2, 26)
22	$N^+ + O_2 \rightarrow N + O_2^+$	$k = 3.0 * 10^{-10}$	(26)
23	$N^+ + O_2 \rightarrow O^+ + NO$	$k = 3.6 * 10^{-11}$	(26)
24	$N^+ + H_2O \rightarrow H_2O^+ + N$	$k = 2.4 * 10^{-9}$	(26)
25	$N^+ + H_2O \rightarrow NO^+ + H_2$	$k = 4.0 * 10^{-10}$	(26)
26	$N^+ + CO_2 \rightarrow CO_2^+ + N$	$k = 1.3 * 10^{-9}$	(26)
27	$N^+ + CO_2 \rightarrow CO^+ + NO$	$k = 2.5 * 10^{-10}$	(26, 59)
28	$N^+ + NO \rightarrow NO^+ + N$	$k = 5.1 * 10^{-10}$	(26)
29	$N^+ + NO \rightarrow N_2^+ + O$	$k = 5.0 * 10^{-11}$	(26)
30	$N^+ + NO_2 \rightarrow NO^+ + NO$	$k = 5.0 * 10^{-10}$	(16)
31	$N^+ + NO_2 \rightarrow NO_2^+ + N$	$k = 3.0 * 10^{-10}$	(16)
32	$N^+ + NH_3 \rightarrow NH_3^+ + N$	$k = 1.7 * 10^{-9}$	(8, 26)
33	$N^+ + O_3 \rightarrow NO^+ + O_2$	$k = 5.0 * 10^{-10}$	(16)
34	$N^+ + N_2O \rightarrow NO^+ + N_2$	$k = 5.5 * 10^{-10}$	(26)
35	$N^+ + H_2 \rightarrow H_2^+ + N$	$k = 2.0 * 10^{-10}$	(26)
36	$N^+ + CO \rightarrow CO^+ + N$	$k = 4.9 * 10^{-10}$	(26)
37	$N^+ + OH \rightarrow OH^+ + N$	$k = 3.4 * 10^{-10}$	(16, 59)
38	$N^+ + OH \rightarrow NO^+ + H$	$k = 3.4 * 10^{-10}$	(59)

39	$N^+ + H \rightarrow H^+ + N$	$k = 3.0 * 10^{-10}$	(16)
40	$N^+ + O \rightarrow O^+ + N$	$k = 1.0 * 10^{-12}$	(16)
41	$N^+ + O + M \rightarrow NO^+ + M$	$k = 1.0 * 10^{-29} * (300/T)$	(16)
42	$N^+ + N + M \rightarrow N_2^+ + M$	$k = 1.0 * 10^{-29} * (300/T)$	(16)
43	$N^+ + N_2 + M \rightarrow N_3^+ + M$	$k = 1.8 * 10^{-29} * (300/T)$	(16)
44	$N_3^+ + O_2 \rightarrow NO^+ + O + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
45	$N_3^+ + NO \rightarrow NO^+ + N + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
46	$N_3^+ + NO_2 \rightarrow NO_2^+ + N + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
47	$N_3^+ + N \rightarrow N_2^+ + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
48	$N_4^+ + H_2O \rightarrow H_2O^+ + 2\ N_2$	$k = 3.0 * 10^{-10}$	(16)
49	$N_4^+ + CO_2 \rightarrow CO_2^+ + 2\ N_2$	$k = 3.0 * 10^{-10}$	(16)
50	$N_4^+ + N_2O \rightarrow N_2O^+ + 2\ N_2$	$k = 3.0 * 10^{-10}$	(16)
51	$N_4^+ + OH \rightarrow OH^+ + 2\ N_2$	$k = 3.0 * 10^{-10}$	(16)
52	$O_2^+ + N_2 \rightarrow NO^+ + NO$	$k = 1.0 * 10^{-16}$	(16)
53	$O_2^+ + NO \rightarrow NO^+ + O_2$	$k = 3.5 * 10^{-10}$	(26, 75)

54	$O_2^+ + NO_2 \rightarrow NO_2^+ + O_2$	$k = 6.0 * 10^{-10}$	(16)
55	$O_2^+ + NH_3 \rightarrow NH_3^+ + O_2$	$k = 2.4 * 10^{-9}$	(26)
56	$O_2^+ + N_2O_5 \rightarrow NO_2^+ + NO_3 + O_2$	$k = 8.8 * 10^{-10}$	(68)
57	$O_2^+ + N \rightarrow NO^+ + O$	$k = 1.8 * 10^{-10}$	(4, 55)
58	$O_2^+ + 2\ O_2 \rightarrow O_4^+ + O2$	$k = 2.8 * 10^{-30} * (300/T)$	(16)
59	$O_2^+ + H_2O + M \rightarrow O_2^+(H_2O) + M$	$k = 2.8 * 10^{-28} * (300/T)$	(16, 65)
60	$O^+ + N_2 \rightarrow N_2^+ + O$	$k = 9.0 * 10^{-11} * T^{-0.7}$	(2, 59)
61	$O^+ + N_2 \rightarrow NO^+ + N$	$k = 1.2 * 10^{-12} + 5.4 * 10^{-29} * (300/T) * M$	(16, 26)
62	$O^+ + O_2 \rightarrow O_2^+ + O$	$k = 6.6 * 10^{-10} * T^{-0.55}$	(26, 59)
63	$O^+ + H_2O \rightarrow H_2O^+ + O$	$k = 2.7 * 10^{-9}$	(26, 59)
64	$O^+ + CO_2 \rightarrow O_2^+ + CO$	$k = 1.0 * 10^{-9}$	(7, 59)
65	$O^+ + NO \rightarrow NO^+ + O$	$k = 1.0 * 10^{-12}$	(26)
66	$O^+ + NO_2 \rightarrow NO_2^+ + O$	$k = 1.6 * 10^{-9}$	(16)
67	$O^+ + NO_2 \rightarrow NO^+ + O_2$	$k = 5.0 * 10^{-10}$	(16)
68	$O^+ + SO_2 \rightarrow O_2^+ + SO$	$k = 8.0 * 10^{-10}$	(26)
69	$O^+ + NH_3 \rightarrow NH_3^+ + O$	$k = 1.2 * 10^{-9}$	(59)
70	$O^+ + O_3 \rightarrow O_2^+ + O_2$	$k = 1.1 * 10^{-10}$	(16)
71	$O^+ + N_2O \rightarrow N_2O^+ + O$	$k = 5.0 * 10^{-10}$	(16, 26)
72	$O^+ + H_2 \rightarrow OH^+ + H$	$k = 1.8 * 10^{-9}$	(16, 59)
73	$O^+ + OH \rightarrow OH^+ + O$	$k = 3.3 * 10^{-10}$	(16, 59)

74	$O^+ + OH \rightarrow H^+ + O_2$	$k = 2.7 * 10^{-11} * (T/300)^{0.13}$	(16)
75	$O^+ + OH \rightarrow O_2^+ + H$	$k = 3.6 * 10^{-10}$	(59)
76	$O^+ + H \rightarrow H^+ + O$	$k = 6.8 * 10^{-11}$	(16, 59)
77	$O_4^+ + H_2O \rightarrow O_2^+(H_2O) + O_2$	$k = 1.8 * 10^{-9}$	(2, 65)
78	$O_4^+ + NO \rightarrow NO^+ + 2\ O_2$	$k = 5.0 * 10^{-10}$	(16)
79	$O_4^+ + NO_2 \rightarrow NO_2^+ + 2\ O_2$	$k = 3.0 * 10^{-10}$	(16)
80	$O_4^+ + O \rightarrow O_2^+ + O_3$	$k = 3.0 * 10^{-10}$	(16)
81	$O_2^+(H_2O) + H_2O \rightarrow H_3O^+ + OH + O_2$	$k = 2.0 * 10^{-10}$	(2, 16, 65)
82	$O_2^+(H_2O) + H_2O \rightarrow H_3O^+(OH) + O_2$	$k = 1.5 * 10^{-9}$	(2, 16, 65)
83	$O_2^+(H_2O) + NO_2 \rightarrow NO_2^+ + H_2O + O_2$	$k = 3.0 * 10^{-10}$	(16)
84	$O_2^+(H_2O) + NO \rightarrow NO^+ + H_2O + O_2$	$k = 1.0 * 10^{-10}$	(16)
85	$H_2O^+ + O_2 \rightarrow O_2^+ + H_2O$	$k = 2.6 * 10^{-10}$	(26, 59)
86	$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	$k = 1.7 * 10^{-9}$	(3, 26, 59)
87	$H_2O^+ + NO \rightarrow NO^+ + H_2O$	$k = 6.0 * 10^{-10}$	(26, 59)
88	$H_2O^+ + NO_2 \rightarrow NO_2^+ + H_2O$	$k = 3.0 * 10^{-10}$	(16)
89	$H_2O^+ + NH_3 \rightarrow NH_3^+ + H_2O$	$k = 2.2 * 10^{-9}$	(26)
90	$H_2O^+ + NH_3 \rightarrow NH_4^+ + OH$	$k = 9.0 * 10^{-10}$	(26)
91	$H_2O^+ + H_2 \rightarrow H_3O^+ + H$	$k = 8.7 * 10^{-10}$	(16, 26, 59)
92	$H_2O^+ + OH \rightarrow H_3O^+ + O$	$k = 6.9 * 10^{-10}$	(26)
93	$H_2O^+ + O \rightarrow O_2^+ + H_2$	$k = 5.5 * 10^{-11}$	(26, 59)

94	$H_2O^+ + N \rightarrow NO^+ + H_2$	$k = 9.0 * 10^{-11}$	(26)
95	$H_3O^+ + N_2O_5 \rightarrow NO_2^+(H_2O) + HNO_3$	$k = 5.5 * 10^{-10}$	(68, 78)
96	$H_3O^+ + N_2O_5 \rightarrow NO_2^+ + H_2O + HNO_3$	$k = 5.5 * 10^{-10}$	(68, 78)
97	$H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$	$k = 2.2 * 10^{-9}$	(26)
98	$H_3O^+ + HNO_3 \rightarrow NO_2^+(H_2O) + H_2O$	$k = 1.6 * 10^{-9}$	(62)
99	$H_3O^+ + OH + O_2 \rightarrow O_2^+(H_2O) + H_2O$	$k = 1.6 * 10^{-27} * (T/300)^{0.55}$	(16)
100	$H_3O^+ + OH + M \rightarrow H_3O^+(OH) + M$	$k = 5.4 * 10^{-25} * (300/T)^{0.7}$	(16)
101	$H_3O^+ + H_2O + M \rightarrow H_3O^+(H_2O) + M$	$k = 3.7 * 10^{-27} * (300/T)$	(16)
102	$H_3O^+(OH) + H_2O \rightarrow H_3O^+ + H_2O + OH$	$k = 1.4 * 10^{-9}$	(2)
103	$H_3O^+(OH) + H_2O \rightarrow H_3O^+(H_2O) + OH$	$k = 3.0 * 10^{-9}$	(65)
104	$H_3O^+(OH) + NO \rightarrow NO^+ + 2\ H_2O$	$k = 3.0 * 10^{-10}$	(16)
105	$H_3O^+(OH) + NO_2 \rightarrow NO_2^+ + 2\ H_2O$	$k = 3.0 * 10^{-10}$	(16)
106	$H_3O^+(H_2O) + H_2O + M \rightarrow H_3O^+(H_2O)_2 + M$	$k = 3.0 * 10^{-27} * (300/T)$	(16, 60)
107	$H_3O^+(H_2O) + OH \rightarrow H_3O^+(OH) + H_2O$	$k = 2.1 * 10^{-11} * (300/T)^{1.46} * \exp(-4503/T)$	(16)
108	$H_3O^+(H_2O)_2 + M \rightarrow H_3O^+(H_2O) + H_2O + M$	$k = 5.9 * 10^{-1} * (T/300)^{0.54} * \exp(-11220/T)$	(16)
109	$H_3O^+(H_2O)_2 + HNO_2 \rightarrow NO^+(H_2O)_3 + H_2O$	$k = 1.1 * 10^{-8} * (300/T)^{2.6}$	(16)
110	$CO_2^+ + O_2 \rightarrow O_2^+ + CO_2$	$k = 6.5 * 10^{-9} * T^{-0.78}$	(59)
111	$CO_2^+ + H_2O \rightarrow H_2O^+ + CO_2$	$k = 1.7 * 10^{-9}$	(59)
112	$CO_2^+ + NO \rightarrow NO^+ + CO_2$	$k = 1.2 * 10^{-10}$	(26)
113	$CO_2^+ + NO_2 \rightarrow NO_2^+ + CO_2$	$k = 3.0 * 10^{-10}$	(16)

114 $CO_2^+ + SO_2 \rightarrow SO_2^+ + CO_2$ $k = 1.5 * 10^{-9}$ (26)

115 $CO_2^+ + NH_3 \rightarrow NH_3^+ + CO_2$ $k = 1.9 * 10^{-9}$ (26)

116 $CO_2^+ + N_2O \rightarrow N_2O^+ + CO_2$ $k = 3.0 * 10^{-10}$ (16)

117 $CO_2^+ + OH \rightarrow OH^+ + CO_2$ $k = 3.0 * 10^{-10}$ (16)

118 $CO_2^+ + O \rightarrow CO + O_2^+$ $k = 1.3 * 10^{-10}$ (7, 59)

119 $CO_2^+ + O \rightarrow O^+ + CO_2$ $k = 1.3 * 10^{-10}$ (16, 59)

120 $CO_2^+ + H \rightarrow H^+ + CO_2$ $k = 1.9 * 10^{-10}$ (16, 59)

121 $CO^+ + O_2 \rightarrow O_2^+ + CO$ $k = 1.0 * 10^{-10}$ (39)

122 $CO^+ + H_2O \rightarrow H_2O^+ + CO$ $k = 1.3 * 10^{-10}$ (16, 59)

123 $CO^+ + CO_2 \rightarrow CO_2^+ + CO$ $k = 8.5 * 10^{-10}$ (3, 16, 59)

124 $CO^+ + NO \rightarrow NO^+ + CO$ $k = 3.3 * 10^{-10}$ (7)

125 $CO^+ + NO_2 \rightarrow NO_2^+ + CO$ $k = 3.0 * 10^{-10}$ (16)

126 $CO^+ + SO_2 \rightarrow SO_2^+ + CO$ $k = 2.0 * 10^{-10}$ (26)

127 $CO^+ + NH_3 \rightarrow NH_3^+ + CO$ $k = 2.0 * 10^{-9}$ (26)

128 $CO^+ + N_2O \rightarrow N_2O^+ + CO$ $k = 3.0 * 10^{-10}$ (16)

129 $CO^+ + OH \rightarrow OH^+ + CO$ $k = 2.5 * 10^{-10}$ (16, 59)

130 $CO^+ + OH \rightarrow CO_2^+ + H$ $k = 2.1 * 10^{-10}$ (59)

131 $CO^+ + O \rightarrow O^+ + CO$ $k = 1.4 * 10^{-10}$ (7)

132 $CO^+ + H \rightarrow H^+ + CO$ $k = 3.0 * 10^{-10}$ (16)

133 $C^+ + O_2 \rightarrow CO^+ + O$ $k = 3.0 * 10^{-10}$ (39)

134	$C^+ + O_2 \rightarrow O^+ + CO$	$k = 6.0 * 10^{-10}$	(39)
135	$C^+ + CO_2 \rightarrow CO^+ + CO$	$k = 1.5 * 10^{-9}$	(3, 26)
136	$C^+ + NO \rightarrow N^+ + CO$	$k = 7.0 * 10^{-10}$	(26)
137	$C^+ + OH \rightarrow CO^+ + H$	$k = 7.7 * 10^{-10}$	(59)
138	$H^+ + O_2 \rightarrow O_2^+ + H$	$k = 1.2 * 10^{-9}$	(26)
139	$H^+ + H_2O \rightarrow H_2O^+ + H$	$k = 8.2 * 10^{-9}$	(26)
140	$H^+ + H_2O + M \rightarrow H_3O^+ + M$	$k = 2.0 * 10^{-27}$	(3, 16)
141	$H^+ + CO_2 \rightarrow CO_2^+ + H$	$k = 1.2 * 10^{-9} * \exp(-1942/T)$	(16)
142	$H^+ + NO \rightarrow NO^+ + H$	$k = 7.0 * 10^{-10}$	(26, 59)
143	$H^+ + NO_2 \rightarrow NO_2^+ + H$	$k = 3.0 * 10^{-10}$	(16)
144	$H^+ + NH_3 \rightarrow NH_3^+ + H$	$k = 5.2 * 10^{-9}$	(26)
145	$H^+ + N_2O \rightarrow N_2O^+ + H$	$k = 3.0 * 10^{-10}$	(16)
146	$H^+ + OH \rightarrow OH^+ + H$	$k = 2.0 * 10^{-9}$	(16, 59)
147	$H^+ + O \rightarrow O^+ + H$	$k = 3.8 * 10^{-10}$	(26)
148	$H_2^+ + O_2 \rightarrow O_2^+ + H_2$	$k = 8.0 * 10^{-10}$	(26)
149	$H_2^+ + O_2 \rightarrow H_2O^+ + O$	$k = 1.9 * 10^{-9}$	(26)
150	$H_2^+ + H_2O \rightarrow H_2O^+ + H_2$	$k = 3.9 * 10^{-9}$	(26)
151	$H_2^+ + H_2O \rightarrow H_3O^+ + H$	$k = 3.4 * 10^{-9}$	(26)
152	$H_2^+ + CO_2 \rightarrow CO_2^+ + H_2$	$k = 1.4 * 10^{-9}$	(26)

153	$H_2^+ + CO_2 \rightarrow CO^+ + H_2O$	$k = 1.4 * 10^{-9}$	(26)
154	$H_2^+ + CO \rightarrow CO^+ + H_2$	$k = 6.44 * 10^{-10}$	(26)
155	$H_2^+ + NO \rightarrow NO^+ + H_2$	$k = 1.1 * 10^{-9}$	(26)
156	$H_2^+ + NH_3 \rightarrow NH_3^+ + H_2$	$k = 5.7 * 10^{-9}$	(26)
157	$H_2^+ + OH \rightarrow H_2O^+ + H$	$k = 7.5 * 10^{-10}$	(59)
158	$H_2^+ + OH \rightarrow OH^+ + H_2$	$k = 7.5 * 10^{-10}$	(59)
159	$H_2^+ + H \rightarrow H^+ + H_2$	$k = 6.4 * 10^{-10}$	(26)
160	$OH^+ + O_2 \rightarrow O_2^+ + OH$	$k = 2.0 * 10^{-10}$	(26)
161	$OH^+ + H_2O \rightarrow H_3O^+ + O$	$k = 1.5 * 10^{-9}$	(3, 16)
162	$OH^+ + H_2O \rightarrow H_2O^+ + OH$	$k = 1.5 * 10^{-9}$	(26)
163	$OH^+ + NO \rightarrow NO^+ + OH$	$k = 4.6 * 10^{-10}$	(26)
164	$OH^+ + NO_2 \rightarrow NO_2^+ + OH$	$k = 3.0 * 10^{-10}$	(16)
165	$OH^+ + NH_3 \rightarrow NH_3^+ + OH$	$k = 1.2 * 10^{-9}$	(26)
166	$OH^+ + NH_3 \rightarrow NH_4^+ + O$	$k = 1.2 * 10^{-9}$	(26)
167	$OH^+ + N_2O \rightarrow N_2O^+ + OH$	$k = 5.0 * 10^{-10}$	(16, 26)
168	$OH^+ + N_2O \rightarrow NO^+ + HNO$	$k = 1.7 * 10^{-10}$	(16, 26)
169	$OH^+ + H_2 \rightarrow H_2O^+ + H$	$k = 1.3 * 10^{-9}$	(16, 59)
170	$OH^+ + OH \rightarrow H_2O^+ + O$	$k = 7.0 * 10^{-10}$	(59)
171	$NO^+ + H_2O + M \rightarrow NO^+(H_2O) + M$	$k = 1.5 * 10^{-28} * (300/T)$	(16, 65)
172	$NO^+ + O_3 \rightarrow NO_2^+ + O_2$	$k = 1.0 * 10^{-14}$	(16), but not in (26)

173	$NO^+ + N_2O_5 \rightarrow NO_2^+ + 2\ NO_2$	$k = 5.9 * 10^{-10}$	(68)
174	$NO^+ + N + M \rightarrow N_2O^+ + M$	$k = 1.0 * 10^{-29} * (300/T)$	(16)
175	$NO^+(H_2O) + H_2O + M \rightarrow NO^+(H_2O)_2 + M$	$k = 1.1 * 10^{-27} * (300/T)$	(16)
176	$NO^+(H_2O) + NO_2 \rightarrow NO_2^+(H_2O) + NO$	$k = 2.0 * 10^{-15}$	(62)
177	$NO^+(H_2O) + NH_3 \rightarrow NH_4^+ + HNO_2$	$k = 1.0 * 10^{-9}$	(66)
178	$NO^+(H_2O)_2 + M \rightarrow NO^+(H_2O) + H_2O + M$	$k = 1.0 * 10^{-14}$	(65)
179	$NO^+(H_2O)_2 + H_2O + M \rightarrow NO^+(H_2O)_3 + M$	$k = 2.0 * 10^{-27} * (300/T)$	(16, 65)
180	$NO^+(H_2O)_2 + NH_3 \rightarrow NH_4^+ + HNO_2 + H_2O$	$k = 1.0 * 10^{-9}$	NH_4^+/H_2O clusters neglected (66)
181	$NO^+(H_2O)_3 + M \rightarrow NO^+(H_2O)_2 + H_2O + M$	$k = 1.5 * 10^{-12}$	(16, 65)
182	$NO^+(H_2O)_3 + H_2O \rightarrow H_3O^+(H_2O)_2 + HNO_2$	$k = 2.0 * 10^{-6} * \exp(-3000/T)$	(16, 65)
183	$NO^+(H_2O)_3 + NH_3 \rightarrow NH_4^+ + HNO_2 + 2\ H_2O$	$k = 1.0 * 10^{-9}$	NH_4^+/H_2O clusters neglected (66)
184	$NO_2^+ + NO \rightarrow NO^+ + NO_2$	$k = 2.9 * 10^{-10}$	(16)
185	$NO_2^+ + H_2O + N_2 \rightarrow NO_2^+(H_2O) + N2$	$k = 5.0 * 10^{-28}$	(62)
186	$NO_2^+(H_2O) + NH_3 \rightarrow NH_4^+ + HNO_3$	$k = 6.4 * 10^{-10}$	(62)
187	$NO_2^+(H_2O) + N_2 \rightarrow NO_2^+ + H_2O + N2$	$k = 5.0 * 10^{-15}$	(62)
188	$NO_2^+(H_2O) + NO \rightarrow NO^+(H_2O) + NO_2$	$k = 3.1 * 10^{-11}$	(62)
189	$NO_2^+(H_2O) + H_2O + N_2 \rightarrow NO_2^+(H_2O)_2H + N2$	$k = 2.0 * 10^{-27}$	(62)
190	$NO_2^+(H_2O)_2H + H_2O \rightarrow H_3O^+(H_2O) + HNO_3$	$k = 2.0 * 10^{-10}$	(62)
191	$N_2O^+ + O_2 \rightarrow O_2^+ + N_2O$	$k = 2.3 * 10^{-10}$	(16, 26)
192	$N_2O^+ + O_2 \rightarrow NO^+ + NO_2$	$k = 4.0 * 10^{-11}$	(26)

193	$N_2O^+ + H_2O \rightarrow H_2O^+ + N_2O$	$k = 3.0 * 10^{-10}$	(16)
194	$N_2O^+ + NO \rightarrow NO^+ + N_2O$	$k = 2.0 * 10^{-10}$	(16, 26)
195	$N_2O^+ + NO_2 \rightarrow NO_2^+ + N_2O$	$k = 2.2 * 10^{-10}$	(16, 26)
196	$N_2O^+ + NO_2 \rightarrow NO^+ + N_2 + O_2$	$k = 3.3 * 10^{-10}$	(26)
197	$N_2O^+ + N_2O \rightarrow NO^+ + NO + N_2$	$k = 1.2 * 10^{-11}$	(26)
198	$N_2O^+ + CO \rightarrow CO_2^+ + N_2$	$k = 1.0 * 10^{-10}$	(26)
199	$N_2O^+ + OH \rightarrow OH^+ + N_2O$	$k = 9.2 * 10^{-11} * (300/T)^{0.46} * \exp(-3326/T)$	(16)
200	$SO_2^+ + O_2 \rightarrow O_2^+ + SO_2$	$k = 2.8 * 10^{-10}$	(26)
201	$SO_2^+ + NO \rightarrow NO^+ + SO_2$	$k = 7.0 * 10^{-11}$	(26)
202	$NH_3^+ + H_2O \rightarrow NH_4^+ + OH$	$k = 6.0 * 10^{-11}$	(26, 59)
203	$NH_3^+ + NO \rightarrow NO^+ + NH_3$	$k = 7.3 * 10^{-10}$	(26)
204	$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$	$k = 2.0 * 10^{-9}$	(3, 26)
205	$NH_3^+ + OH \rightarrow NH_4^+ + O$	$k = 7.0 * 10^{-10}$	(59)
206	$NH_3^+ + NH_2 \rightarrow NH_4^+ + NH$	$k = 1.0 * 10^{-11}$	(59)

Table III. Negative ion-neutral reactions

207	$e^-(\text{hot}) \rightarrow e^-(\text{thermal})$	$k = 1.0 * 10^{+9}$		acc. to (60)
208	$e^- + 2\,O_2 \rightarrow O_2^- + O_2^*$	$k = 1.2 * 10^{-29} * (300/T)^{1.38} * \exp(-6602/T)$		(16)
209	$e^- + O_2 + M \rightarrow O_2^- + M$	$k = 3.0 * 10^{-31}$	M is not O_2	(5, 16)
210	$e^- + NO + M \rightarrow NO^- + M$	$k = 8.0 * 10^{-31}$		(16)
211	$e^- + NO_2 + M \rightarrow NO_2^- + M$	$k = 1.5 * 10^{-30}$		(16)
212	$e^- + HNO_3 \rightarrow NO_2^- + OH$	$k = 5.0 * 10^{-8}$		(62)
213	$e^- + O_3 \rightarrow O^- + O_2$	$k = 9.0 * 10^{-12} * (300/T)^{1.5}$		(5, 16)
214	$e^- + O_3 + M \rightarrow O_3^- + M$	$k = 1.0 * 10^{-30}$		(16)
215	$e^- + NO_3 + M \rightarrow NO_3^- + M$	$k = 1.0 * 10^{-30}$		(16)
216	$O^- + O_2 + M \rightarrow O_3^- + M$	$k = 1.1 * 10^{-30} * (300/T)$		(16)
217	$O^- + O_2^* \rightarrow e^- + O_3$	$k = 3.0 * 10^{-10}$		(16)
218	$O^- + CO_2 + M \rightarrow CO_3^- + M$	$k = 8.0 * 10^{-29} * (300/T)$		(16)
219	$O^- + NO \rightarrow e^- + NO_2$	$k = 3.1 * 10^{-10} * (300/T)^{0.83}$		(16, 69)
220	$O^- + NO + M \rightarrow NO_2^- + M$	$k = 1.0 * 10^{-29} * (300/T)$		(16)
221	$O^- + NO_2 \rightarrow NO_2^- + O$	$k = 1.2 * 10^{-9}$		(16)
222	$O^- + N_2O \rightarrow NO^- + NO$	$k = 2.3 * 10^{-10}$		(16)
223	$O^- + O_3 \rightarrow O_3^- + O$	$k = 6.5 * 10^{-10}$		(5, 16)
224	$O^- + CO \rightarrow e^- + CO_2$	$k = 6.0 * 10^{-10} * (300/T)^{0.32}$		(16)
225	$O^- + H_2 \rightarrow e^- + H_2O$	$k = 6.5 * 10^{-10} * (300/T)^{0.19}$		(16)

226	$O^- + O \rightarrow e^- + O_2$	$k = 1.9 * 10^{-10}$	(5, 16)
227	$O^- + N \rightarrow e^- + NO$	$k = 2.0 * 10^{-10}$	(16)
228	$O^- + NO_3 \rightarrow NO_3^- + O$	$k = 3.0 * 10^{-10}$	(16)
229	$O_2^- + O_2 + M \rightarrow O_4^- + M$	$k = 3.5 * 10^{-31} * (300/T)$	(16)
230	$O_2^- + O_2^* \rightarrow e^- + 2\ O_2$	$k = 2.0 * 10^{-10}$	(16)
231	$O_2^- + H_2O + M \rightarrow O_2^-(H_2O) + M$	$k = 3.0 * 10^{-28} * (300/T)$	(16)
232	$O_2^- + NO_2 \rightarrow NO_2^- + O_2$	$k = 8.0 * 10^{-10}$	(16)
233	$O_2^- + HNO_3 \rightarrow NO_3^- + HO_2$	$k = 2.8 * 10^{-10}$	(62)
234	$O_2^- + O_3 \rightarrow O_3^- + O_2$	$k = 5.0 * 10^{-10}$	(5, 16, 78)
235	$O_2^- + H_2 \rightarrow e^- + H_2O_2$	$k = 1.0 * 10^{-9}$	(16)
236	$O_2^- + O \rightarrow O^- + O_2$	$k = 1.5 * 10^{-10}$	(5, 78)
237	$O_2^- + O \rightarrow e^- + O_3$	$k = 1.5 * 10^{-10}$	(5, 78)
238	$O_2^- + H \rightarrow e^- + HO_2$	$k = 1.0 * 10^{-9}$	(16)
239	$O_2^- + N \rightarrow e^- + NO_2$	$k = 5.0 * 10^{-10}$	(16)
240	$O_2^- + NO_3 \rightarrow NO_3^- + O_2$	$k = 5.0 * 10^{-10}$	(16)
241	$O_2^-(H_2O) + NO \rightarrow NO_3^- + H_2O$	$k = 3.0 * 10^{-10}$	(16)
242	$O_2^-(H_2O) + NO_2 \rightarrow NO_2^- + O_2 + H_2O$	$k = 3.0 * 10^{-10}$	(16)
243	$O_2^-(H_2O) + O_3 \rightarrow O_3^- + O_2 + H_2O$	$k = 8.0 * 10^{-10}$	(67)
244	$O_2^-(H_2O) + O \rightarrow O^- + O_2 + H_2O$	$k = 3.0 * 10^{-10}$	(16)
245	$O_2^-(H_2O) + NO_3 \rightarrow NO_3^- + O_2 + H_2O$	$k = 3.0 * 10^{-10}$	(16)

246	$O_2^-(H_2O) + N \rightarrow e^- + NO_2 + H_2O$	$k = 1.0 * 10^{-10}$	(16)
247	$O_3^- + CO_2 \rightarrow CO_3^- + O_2$	$k = 4.8 * 10^{-10}$	(5, 16, 78)
248	$O_3^- + NO \rightarrow NO_2^- + O_2$	$k = 1.0 * 10^{-11}$	(16)
249	$O_3^- + NO_2 \rightarrow NO_2^- + O_3$	$k = 2.8 * 10^{-10}$	(16)
250	$O_3^- + NO_2 \rightarrow NO_3^- + O_2$	$k = 2.0 * 10^{-11}$	(16)
251	$O_3^- + SO_2 \rightarrow SO_3^- + O_2$	$k = 1.7 * 10^{-9}$	(81)
252	$O_3^- + O \rightarrow O_2^- + O_2$	$k = 2.5 * 10^{-10}$	(78)
253	$O_3^- + O \rightarrow e^- + 2\ O_2$	$k = 1.0 * 10^{-11}$	(16)
254	$O_3^- + NO_3 \rightarrow NO_3^- + O_3$	$k = 5.0 * 10^{-10}$	(16)
255	$NO^- + M \rightarrow e^- + NO + M$	$k = 2.1 * 10^{-11} * (300/T)^{1.54} * \exp(-278/T)$	(16)
256	$NO^- + O_2 \rightarrow O_2^- + NO$	$k = 5.0 * 10^{-10}$	(16)
257	$NO^- + NO_2 \rightarrow NO_2^- + NO$	$k = 3.0 * 10^{-10}$	(16)
258	$NO^- + O_3 \rightarrow O_3^- + NO$	$k = 3.0 * 10^{-10}$	(16)
259	$NO^- + O \rightarrow O^- + NO$	$k = 3.0 * 10^{-10}$	(16)
260	$NO^- + NO_3 \rightarrow NO_3^- + NO$	$k = 3.0 * 10^{-10}$	(16)
261	$NO_2^- + NO_2 \rightarrow NO_3^- + NO$	$k = 2.0 * 10^{-13}$	(5, 16, 62)
262	$NO_2^- + HNO_3 \rightarrow NO_3^- + HNO_2$	$k = 1.6 * 10^{-9}$	(8, 62)
263	$NO_2^- + N_2O_5 \rightarrow NO_3^- + 2\ NO_2$	$k = 6.5 * 10^{-10}$	(67)
264	$NO_2^- + O_3 \rightarrow NO_3^- + O_2$	$k = 5.0 * 10^{-11}$	(5, 16, 78)
265	$NO_2^- + NO_3 \rightarrow NO_3^- + NO_2$	$k = 5.0 * 10^{-10}$	(16)

266	$NO_3^- + NO \rightarrow NO_2^- + NO_2$	$k = 4.3 * 10^{-11} * (300/T)^{0.35} * \exp(-3788/T)$	(16)
267	$NO_3^- + O + CO_2 \rightarrow CO_3^- + NO_3$	$k = 8.2 * 10^{-34} * (300/T)^{1.16} * \exp(-2619/T)$	(16)
268	$CO_3^- + NO \rightarrow NO_2^- + CO_2$	$k = 1.0 * 10^{-11}$	(5, 16, 78)
269	$CO_3^- + NO_2 \rightarrow NO_3^- + CO_2$	$k = 2.0 * 10^{-10}$	(5, 78)
270	$CO_3^- + HNO_3 \rightarrow NO_3^- + OH + CO_2$	$k = 8.0 * 10^{-10}$	(62)
271	$CO_3^- + N_2O_5 \rightarrow NO_3^- + NO_3 + CO_2$	$k = 2.8 * 10^{-10}$	(67)
272	$CO_3^- + SO_2 \rightarrow SO_3^- + CO_2$	$k = 2.3 * 10^{-10}$	(81)
273	$CO_3^- + O \rightarrow O_2^- + CO_2$	$k = 1.1 * 10^{-10}$	(78)
274	$CO_3^- + NO_3 \rightarrow NO_3^- + CO_2 + O$	$k = 3.0 * 10^{-10}$	(16)
275	$SO_3^- + H_2O \rightarrow e^- + H_2SO_4$	$k = 2.0 * 10^{-11}$	(81)

Table IV. Ionic recombination reactions in the gas phase

276	$N_2^+ + e^- \rightarrow N + N(^2D)$	$k = 2.2 * 10^{-7} * (300/T)^{0.39}$ $+ 6.0 * 10^{-27} * (300/T)^{2.5} * M$	(2, 16)
277	$N_2^+ + e^- \rightarrow N_2$	$k = 4.0 * 10^{-12} * (300/T)^{0.7}$ $+ 6.0 * 10^{-27} * (300/T)^{2.5} * M$	(16)
278	$N_2^+ + O_2^- \rightarrow N_2 + O_2$	$k = 1.6 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
279	$N_2^+ + O^- \rightarrow N_2 + O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
280	$N_2^+ + O_3^- \rightarrow N_2O + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
281	$N_2^+ + NO^- \rightarrow N_2 + NO$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
282	$N_2^+ + NO_2^- \rightarrow NO_2 + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
283	$N_2^+ + NO_3^- \rightarrow NO_2 + N_2O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
284	$N_2^+ + CO_3^- \rightarrow CO_2 + N_2 + O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

285	$N_2^+ + O_4^- \rightarrow N_2 + 2\ O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
286	$N_2^+ + O_2^-(H_2O) \rightarrow N_2 + O_2 + H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
287	$N^+ + e^- \rightarrow N$	$k = 3.5 * 10^{-12} * (300/T)^{0.7}$ $+ 6.0 * 10^{-27} * (300/T)^{2.5} * M$	(4, 16)
288	$N^+ + O^- \rightarrow N + O$	$k = 2.6 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
289	$N^+ + O_2^- \rightarrow N + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
290	$N^+ + O_3^- \rightarrow NO + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
291	$N^+ + NO^- \rightarrow O + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
292	$N^+ + NO_2^- \rightarrow 2\ NO$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
293	$N^+ + NO_3^- \rightarrow NO + NO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
294	$N^+ + CO_3^- \rightarrow NO + CO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

295	$N^+ + O_2^-(H_2O) \rightarrow NO_2 + H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
296	$N_3^+ + e^- \rightarrow N_2 + N$	$k = 6.0 * 10^{-27} * (300/T)^{2.5} * M$ $+ 7.0 * 10^{-7} * (300/T)$	(16)
297	$N_3^+ + O^- \rightarrow NO + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
298	$N_3^+ + O_2^- \rightarrow NO_2 + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
299	$N_3^+ + O_3^- \rightarrow NO_3 + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
300	$N_3^+ + NO^- \rightarrow N_2 + N_2O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
301	$N_3^+ + NO_2^- \rightarrow O_2 + 2\ N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
302	$N_3^+ + NO_3^- \rightarrow NO + NO_2 + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
303	$N_3^+ + CO_3^- \rightarrow NO + CO_2 + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
304	$N_3^+ + O_2^-(H_2O) \rightarrow N_2 + NO_2 + H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

305	$N_3^+ + O_4^- \rightarrow N_2 + NO_2 + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
306	$N_4^+ + e^- \rightarrow 2\ N_2$	$k = 2.0 * 10^{-6} * (300/T)$ $+ 6.0 * 10^{-27} * (300/T)^{2.5} * M$	(16)
307	$N_4^+ + O_2^- \rightarrow 2\ N_2 + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
308	$N_4^+ + NO^- \rightarrow 2\ N_2 + NO$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
309	$N_4^+ + NO_2^- \rightarrow 2\ N_2 + NO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
310	$N_4^+ + NO_3^- \rightarrow N_2 + NO_2 + N_2O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
311	$N_4^+ + O_2^-(H_2O) \rightarrow 2\ N_2 + H_2O + O_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
312	$N_4^+ + O_4^- \rightarrow 2\ N_2 + 2\ O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
313	$O_2^+ + e^- \rightarrow O + O(^1D)$	$k = 2.1 * 10^{-7} * (300/T)^{0.55}$	(16, 75)
314	$O_2^+ + e^- \rightarrow O_2$	$k = 4.0 * 10^{-12} * (300/T)^{0.7}$ $+ 6.0 * 10^{-27} * (300/T)^{2.5} * M$	(4, 16)

315	$O_2^+ + O^- \rightarrow O_2 + O$	$k = 9.6 * 10^{-8} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
316	$O_2^+ + O_2^- \rightarrow 2\ O_2$	$k = 4.2 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
317	$O_2^+ + O_3^- \rightarrow 2\ O_2 + O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
318	$O_2^+ + NO^- \rightarrow NO + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
319	$O_2^+ + NO_2^- \rightarrow NO_2 + O_2$	$k = 4.1 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
320	$O_2^+ + NO_3^- \rightarrow NO_2 + O_2 + O$	$k = 1.3 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
321	$O_2^+ + CO_3^- \rightarrow CO_2 + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
322	$O_2^+ + O_2^-(H_2O) \rightarrow 2\ O_2 + H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
323	$O^+ + e^- \rightarrow O$	$k = 4.0 * 10^{-12} * (T/300)^{-0.7}$ $+ 6.0 * 10^{-27} * (300/T)^{2.5} * M$	(2, 16)
324	$O^+ + O^- \rightarrow 2\ O$	$k = 2.7 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

325	$O^+ + O_2^- \rightarrow O + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
326	$O^+ + O_3^- \rightarrow 2\ O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
327	$O^+ + NO^- \rightarrow NO + O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
328	$O^+ + NO_2^- \rightarrow NO + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
329	$O^+ + NO_3^- \rightarrow O_2 + NO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
330	$O^+ + CO_3^- \rightarrow O_2 + CO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
331	$O^+ + O_2^-(H_2O) \rightarrow O_3 + H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
332	$O_4^+ + e^- \rightarrow 2\ O_2$	$k = 2.0 * 10^{-6} * (300/T)$ $+ 6.0 * 10^{-27} * (300/T)^{2.5} * M$	(16)
333	$O_4^+ + O^- \rightarrow O_2 + O_3$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
334	$O_4^+ + O_2^- \rightarrow 2\ O_2 + 2\ O$	$k = 2.0 * 10^{-6}$	(2)

335	$O_4^+ + O_2^- \rightarrow 3\ O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
336	$O_4^+ + O_3^- \rightarrow 2\ O_2 + O_3$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
337	$O_4^+ + NO^- \rightarrow 2\ O_2 + NO_3$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
338	$O_4^+ + NO_2^- \rightarrow 2\ O_2 + NO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
339	$O_4^+ + NO_3^- \rightarrow O_2 + NO_2 + O_3$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
340	$O_4^+ + CO_3^- \rightarrow O_2 + CO_2 + O_3$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
341	$O_4^+ + O_2^-(H_2O) \rightarrow 3\ O_2 + H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
342	$O_2^+(H_2O) + e^- \rightarrow H_2O + O_2$	$k = 1.5 * 10^{-6} * (300/T)^{0.2}$ $+ 5.0 * 10^{-26} * (300/T)^{2.5} * M$	(16)
343	$O_2^+(H_2O) + O^- \rightarrow H_2O + O_3$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
344	$O_2^+(H_2O) + O_2^- \rightarrow H_2O + 2\ O_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

345	$O_2^+(H_2O) + O_3^- \rightarrow H_2O + O_2 + O_3$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
346	$O_2^+(H_2O) + O_4^- \rightarrow H_2O + 3\ O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
347	$O_2^+(H_2O) + NO^- \rightarrow H_2O + NO_3$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
348	$O_2^+(H_2O) + NO_2^- \rightarrow H_2O + O_2 + NO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
349	$O_2^+(H_2O) + NO_3^- \rightarrow H_2O + O_3 + NO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
350	$O_2^+(H_2O) + CO_3^- \rightarrow H_2O + O_2 + CO_2 + O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
351	$O_2^+(H_2O) + O_2^-(H_2O) \rightarrow 2\ O_2 + 2\ H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
352	$H_2O^+ + e^- \rightarrow OH + H$	$k = 6.6 * 10^{-6} * T^{-0.5}$	(36)
353	$H_2O^+ + e^- \rightarrow H_2 + O$	$k = 2.4 * 10^{-6} * T^{-0.5}$	(36)
354	$H_2O^+ + e^- \rightarrow 2\ H + O$	$k = 3.0 * 10^{-6} * T^{-0.5}$	(36)
355	$H_2O^+ + e^- + M \rightarrow H_2O + M$	$k = 6.0 * 10^{-27} * (300/T)^{2.5}$	(16)
356	$H_2O^+ + O^- \rightarrow H_2O + O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

357	$H_2O^+ + O_2^- \rightarrow H_2O + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
358	$H_2O^+ + O_3^- \rightarrow H_2O + O_3$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
359	$H_2O^+ + O_4^- \rightarrow 2\ O_2 + H_2O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
360	$H_2O^+ + NO^- \rightarrow NO + H_2O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
361	$H_2O^+ + NO_2^- \rightarrow NO_2 + H_2O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
362	$H_2O^+ + NO_3^- \rightarrow NO_3 + H_2O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
363	$H_2O^+ + CO_3^- \rightarrow H_2O + CO_2 + O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
364	$H_2O^+ + O_2^-(H_2O) \rightarrow O_2 + 2\ H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
365	$H_3O^+ + e^- \rightarrow H_2O + H$	$k = 6.5 * 10^{-7} * (300/T)^{0.5}$ $+ 6.0 * 10^{-27} * (300/T)^{2.5} * M$	(16, 26)
366	$H_3O^+ + e^- \rightarrow OH + 2\ H$	$k = 6.5 * 10^{-7} * (300/T)^{0.5}$	(26)

367	$H_3O^+ + O^- \rightarrow H_2O + OH$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
368	$H_3O^+ + O_2^- \rightarrow H_2O + O_2 + H$	$k = 2.0 * 10^{-6}$	est., (60)
369	$H_3O^+ + O_2^- \rightarrow H_2O + HO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
370	$H_3O^+ + O_3^- \rightarrow H_2O + OH + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
371	$H_3O^+ + NO^- \rightarrow H_2O + H + NO$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
372	$H_3O^+ + NO_2^- \rightarrow H_2O + H + NO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
373	$H_3O^+ + NO_3^- \rightarrow H_2O + OH + NO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
374	$H_3O^+ + CO_3^- \rightarrow H_2O + CO_2 + OH$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
375	$H_3O^+ + O_2^-(H_2O) \rightarrow 2\ H_2O + HO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
376	$H_3O^+(OH) + e^- \rightarrow H_2O + H + OH$	$k = 3.0 * 10^{-6} * (300/T)$	(16)
377	$H_3O^+(OH) + e^- + M \rightarrow 2\ H_2O + M$	$k = 5.0 * 10^{-26} * (300/T)^{2.5}$	(16)

378	$H_3O^+(OH) + O^- \rightarrow H_2O + H_2O_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
379	$H_3O^+(OH) + O_2^- \rightarrow 2\ H_2O + O_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
380	$H_3O^+(OH) + O_3^- \rightarrow H_2O + H_2O_2 + O_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
381	$H_3O^+(OH) + NO^- \rightarrow 2\ H_2O + NO$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
382	$H_3O^+(OH) + NO_2^- \rightarrow 2\ H_2O + NO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
383	$H_3O^+(OH) + NO_3^- \rightarrow H_2O + NO_2 + H_2O_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
384	$H_3O^+(OH) + CO_3^- \rightarrow H_2O + CO_2 + H_2O_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
385	$H_3O^+(OH) + O_2^-(H_2O) \rightarrow 3\ H_2O + O_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
386	$H_3O^+(H_2O) + e^- \rightarrow 2\ H_2O + H$	$k = 2.8 * 10^{-6} * (300/T)^{0.2} + 5.0 * 10^{-26} * (300/T)^{2.5} * M$	(16)
387	$H_3O^+(H_2O) + O^- \rightarrow 2\ H_2O + OH$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

388	$H_3O^+(H_2O) + O_2^- \rightarrow 2\ H_2O + HO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
389	$H_3O^+(H_2O) + O_3^- \rightarrow 2\ H_2O + O_2 + OH$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
390	$H_3O^+(H_2O) + NO^- \rightarrow 2\ H_2O + H + NO$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
391	$H_3O^+(H_2O) + NO_2^- \rightarrow 2\ H_2O + NO_2 + H$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
392	$H_3O^+(H_2O) + NO_3^- \rightarrow 2\ H_2O + NO_2 + OH$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
393	$H_3O^+(H_2O) + CO_3^- \rightarrow 2\ H_2O + CO_2 + OH$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
394	$H_3O^+(H_2O) + O_2^-(H_2O) \rightarrow HO_2 + 3\ H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
395	$H_3O^+(H_2O)_2 + e^- \rightarrow 3\ H_2O + H$	$k = 5.1 * 10^{-6} * (300/T)^{0.2}$ $+ 5.0 * 10^{-26} * (300/T)^{2.5} * M$	(16)
396	$H_3O^+(H_2O)_2 + O^- \rightarrow 3\ H_2O + OH$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
397	$H_3O^+(H_2O)_2 + O_2^- \rightarrow 3\ H_2O + HO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

398	$H_3O^+(H_2O)_2 + O_3^- \rightarrow 3\ H_2O + O_2 + OH$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
399	$H_3O^+(H_2O)_2 + O_4^- \rightarrow 3\ H_2O + O_2 + HO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
400	$H_3O^+(H_2O)_2 + NO^- \rightarrow 3\ H_2O + H + NO$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
401	$H_3O^+(H_2O)_2 + NO_2^- \rightarrow 3\ H_2O + NO_2 + H$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
402	$H_3O^+(H_2O)_2 + NO_3^- \rightarrow 3\ H_2O + NO_2 + OH$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
403	$H_3O^+(H_2O)_2 + CO_3^- \rightarrow 3\ H_2O + CO_2 + OH$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
404	$H_3O^+(H_2O)_2 + O_2^-(H_2O) \rightarrow 4\ H_2O + HO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
405	$CO_2^+ + e^- \rightarrow CO + O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$	(26)
406	$CO_2^+ + e^- + M \rightarrow CO_2 + M$	$k = 6.0 * 10^{-27} * (300/T)^{2.5}$	(26)
407	$CO_2^+ + O^- \rightarrow CO_2 + O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
408	$CO_2^+ + O_2^- \rightarrow CO_2 + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

409	$CO_2^+ + O_3^- \rightarrow CO_2 + O_3$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
410	$CO_2^+ + O_4^- \rightarrow CO_2 + 2\ O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
411	$CO_2^+ + NO^- \rightarrow CO_2 + NO$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
412	$CO_2^+ + NO_2^- \rightarrow CO_2 + NO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
413	$CO_2^+ + NO_3^- \rightarrow CO_2 + NO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
414	$CO_2^+ + CO_3^- \rightarrow 2\ CO_2 + O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
415	$CO_2^+ + O_2^-(H_2O) \rightarrow CO_2 + O_2 + H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
416	$CO^+ + e^- + M \rightarrow CO + M$	$k = 6.0 * 10^{-27} * (300/T)^{2.5}$	(16)
417	$CO^+ + O^- \rightarrow CO + O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
418	$CO^+ + O_2^- \rightarrow CO_2 + O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

419	$CO^+ + O_3^- \rightarrow CO_2 + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
420	$CO^+ + O_4^- \rightarrow CO_2 + O_2 + O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
421	$CO^+ + NO^- \rightarrow CO + NO$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
422	$CO^+ + NO_2^- \rightarrow CO_2 + NO$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
423	$CO^+ + NO_3^- \rightarrow CO_2 + NO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
424	$CO^+ + CO_3^- \rightarrow 2\ CO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
425	$CO^+ + O_2^-(H_2O) \rightarrow CO_2 + O + H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
426	$H^+ + e^- \rightarrow H$	$k = 3.5 * 10^{-12} * (300/T)^{0.7}$ $+ 6.0 * 10^{-27} * (300/T)^{2.5} * M$	(16)
427	$H^+ + O^- \rightarrow H + O$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
428	$H^+ + O_2^- \rightarrow H + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

429	$H^+ + O_3^- \rightarrow OH + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
430	$H^+ + NO^- \rightarrow NO + H$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
431	$H^+ + NO_2^- \rightarrow NO + OH$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
432	$H^+ + NO_3^- \rightarrow NO_2 + OH$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
433	$H^+ + CO_3^- \rightarrow CO_2 + OH$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
434	$H^+ + O_2^-(H_2O) \rightarrow H_2O + HO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
435	$H_2^+ + e^- \rightarrow 2\ H$	$k = 2.3 * 10^{-8} * (100/T)^{0.29}$	(18)
436	$OH^+ + e^- \rightarrow H + O$	$k = 2.0 * 10^{-7}$	(16)
437	$OH^+ + e^- + M \rightarrow OH + M$	$k = 6.0 * 10^{-27} * (300/T)^{2.5}$	(16)
438	$OH^+ + O^- \rightarrow H + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
439	$OH^+ + O_2^- \rightarrow OH + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

440	$OH^+ + O_3^- \rightarrow HO_2 + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
441	$OH^+ + NO^- \rightarrow OH + NO$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
442	$OH^+ + NO_2^- \rightarrow OH + NO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
443	$OH^+ + NO_3^- \rightarrow HNO_2 + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
444	$OH^+ + CO_3^- \rightarrow H + O_2 + CO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
445	$OH^+ + O_2^-(H_2O) \rightarrow OH + O_2 + H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
446	$NO^+ + e^- \rightarrow NO$	$k = 4.0 * 10^{-12} * (300/T)^{0.7}$ $+ 6.0 * 10^{-27} * (300/T)^{2.5} * M$	(4, 16)
447	$NO^+ + e^- + M \rightarrow N + O + M$	$k = 1.0 * 10^{-27}$	(4)
448	$NO^+ + e^- \rightarrow O + N(^2D)$	$k = 4.3 * 10^{-7} * (300/T)^{0.8}$	(16, 55, 75)
449	$NO^+ + O^- \rightarrow O + NO$	$k = 4.9 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
450	$NO^+ + O_2^- \rightarrow NO + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

451	$NO^+ + O_3^- \rightarrow NO + O + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
452	$NO^+ + NO^- \rightarrow O_2 + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
453	$NO^+ + NO_2^- \rightarrow NO_2 + N + O$	$k = 1.0 * 10^{-7}$	(4)
454	$NO^+ + NO_2^- \rightarrow NO + NO_2$	$k = 3.5 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
455	$NO^+ + NO_3^- \rightarrow NO_3 + N + O$	$k = 1.0 * 10^{-7}$	(4)
456	$NO^+ + NO_3^- \rightarrow 2\ NO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
457	$NO^+ + CO_3^- \rightarrow NO_2 + CO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
458	$NO^+ + O_4^- \rightarrow 2\ O_2 + NO$	$k = 4.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
459	$NO^+ + O_2^-(H_2O) \rightarrow NO_3 + H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
460	$NO^+(H_2O) + e^- + M \rightarrow H_2O + NO + M$	$k = 1.0 * 10^{-6} * (300/T)^{0.2} + 5.0 * 10^{-26} * (300/T)^{2.5} * M$	(16)
461	$NO^+(H_2O) + O^- \rightarrow H_2O + NO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

462	$NO^+(H_2O) + O_2^- \rightarrow H_2O + O_2 + NO$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
463	$NO^+(H_2O) + O_3^- \rightarrow H_2O + O_2 + NO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
464	$NO^+(H_2O) + NO^- \rightarrow H_2O + O_2 + N_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
465	$NO^+(H_2O) + NO_2^- \rightarrow H_2O + NO_2 + NO$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
466	$NO^+(H_2O) + NO_3^- \rightarrow H_2O + 2\ NO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
467	$NO^+(H_2O) + CO_3^- \rightarrow H_2O + CO_2 + NO + O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
468	$NO^+(H_2O) + O_2^-(H_2O) \rightarrow NO_3 + 2\ H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
469	$NO^+(H_2O)_2 + e^- + M \rightarrow 2\ H_2O + NO + M$	$k = 2.0 * 10^{-6} * (300/T)^{0.2}$ $+ 5.0 * 10^{-26} * (300/T)^{2.5} * M$	(16)
470	$NO^+(H_2O)_2 + O^- \rightarrow 2\ H_2O + NO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
471	$NO^+(H_2O)_2 + O_2^- \rightarrow 2\ H_2O + O_2 + NO$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

472	$NO^+(H_2O)_2 + O_3^- \rightarrow 2\ H_2O + O_2 + NO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
473	$NO^+(H_2O)_2 + NO^- \rightarrow 2\ H_2O + O_2 + N_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
474	$NO^+(H_2O)_2 + NO_2^- \rightarrow 2\ H_2O + NO + NO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
475	$NO^+(H_2O)_2 + NO_3^- \rightarrow 2\ H_2O + 2\ NO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
476	$NO^+(H_2O)_2 + CO_3^- \Longrightarrow 2\ H_2O + CO_2 + NO + O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
477	$NO^+(H_2O)_2 + O_2^-(H_2O) \rightarrow NO_3 + 3\ H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
478	$NO^+(H_2O)_3 + e^- + M \rightarrow 3\ H_2O + NO + M$	$k = 3.0 * 10^{-6} * (300/T)^{0.2} + 5.0 * 10^{-26} * (300/T)^{2.5} * M$	(16)
479	$NO^+(H_2O)_3 + O^- \rightarrow 3\ H_2O + NO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
480	$NO^+(H_2O)_3 + O_2^- \rightarrow 3\ H_2O + O_2 + NO$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
481	$NO^+(H_2O)_3 + O_3^- \rightarrow 3\ H_2O + O_2 + NO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5} + 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

482	$NO^+(H_2O)_3 + NO^- \rightarrow 3\ H_2O + O_2 + N_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
483	$NO^+(H_2O)_3 + NO_2^- \rightarrow 3\ H_2O + NO_2 + NO$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
484	$NO^+(H_2O)_3 + NO_3^- \rightarrow 3\ H_2O + 2\ NO_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
485	$NO^+(H_2O)_3 + CO_3^- \rightarrow 3\ H_2O + CO_2 + NO + O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
486	$NO^+(H_2O)_3 + O_4^- \rightarrow 3\ H_2O + NO_3 + O_2$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
487	$NO^+(H_2O)_3 + O_2^-(H_2O) \rightarrow 4\ H_2O + NO_3$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
488	$NO_2^+ + e^- \rightarrow NO + O$	$k = 3.0 * 10^{-7} * (300/T)^{0.5}$	(16)
489	$NO_2^+ + e^- + M \rightarrow NO_2 + M$	$k = 6.0 * 10^{-27} * (300/T)^{0.5}$	(16)
490	$NO_2^+ + O^- \rightarrow NO + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
491	$NO_2^+ + O_2^- \rightarrow NO_2 + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
492	$NO_2^+ + O_3^- \rightarrow NO_3 + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

493	$NO_2^+ + NO^- \rightarrow N_2O + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
494	$NO_2^+ + NO_2^- \rightarrow 2\ O_2 + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
495	$NO_2^+ + NO_3^- \rightarrow NO_2 + NO + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
496	$NO_2^+ + CO_3^- \rightarrow NO_3 + CO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
497	$NO_2^+ + O_4^- \rightarrow 2\ O_2 + NO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
498	$NO_2^+ + O_2^-(H_2O) \rightarrow NO_2 + O_2 + H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
499	$N_2O^+ + e^- \rightarrow N_2 + O$	$k = 2.0 * 10^{-7}$	(16)
500	$N_2O^+ + e^- + M \rightarrow N_2O + M$	$k = 6.0 * 10^{-27} * (300/T)^{2.5}$	(16)
501	$N_2O^+ + O^- \rightarrow N_2 + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
502	$N_2O^+ + O_2^- \rightarrow N_2O + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
503	$N_2O^+ + O_3^- \rightarrow N_2 + 2\ O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)

504	$N_2O^+ + NO^- \rightarrow NO_2 + N_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
505	$N_2O^+ + NO_2^- \rightarrow N_2 + NO_3$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
506	$N_2O^+ + NO_3^- \rightarrow 2\ NO + NO_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
507	$N_2O^+ + CO_3^- \rightarrow N_2 + CO_2 + O_2$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
508	$N_2O^+ + O_2^-(H_2O) \rightarrow N_2O + O_2 + H_2O$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	(16)
509	$NH_3^+ + e^- \rightarrow NH_2 + H$	$k = 3.0 * 10^{-7} * (300/T)^{0.5}$	(26)
510	$NH_3^+ + e^- \rightarrow NH + 2\ H$	$k = 3.0 * 10^{-7} * (300/T)^{0.5}$	(26)
511	$NH_4^+ + e^- \rightarrow NH_3 + H$	$k = 3.0 * 10^{-7} * (300/T)^{0.5}$	(26)
512	$NH_4^+ + e^- \rightarrow NH_2 + 2\ H$	$k = 3.0 * 10^{-7} * (300/T)^{0.5}$	(26)
513	$NH_4^+ + NO_2^- \rightarrow NH_3 + NO_2 + H$	$k = 5.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	est., (16)
514	$NH_4^+ + NO_3^- \rightarrow NH_3 + NO_2 + OH$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	est., (16)
515	$NH_4^+ + O_4^- \rightarrow 2\ O_2 + NH_3 + H$	$k = 4.0 * 10^{-7} * (300/T)^{0.5}$ $+ 3.0 * 10^{-25} * (300/T)^{2.5} * M$	est., (16)

Table V. Reactions of excited species

516	$N_2^* + N_2 \rightarrow$ 2 N2	$k = 2.7 * 10^{-11}$	(41, 46)
517	$N_2^* + O_2 \rightarrow N_2 + O_2^*$	$k = 1.0 * 10^{-12}$	(41, 46, 48)
518	$N_2^* + O_2 \rightarrow N_2 + 2\ O$	$k = 2.0 * 10^{-12}$	(48)
519	$N_2^* + O_2 \rightarrow N_2O + O$	$k = 3.0 * 10^{-14}$	(48)
520	$N_2^* + O_2 \rightarrow N_2O + O(^1D)$	$k = 3.0 * 10^{-14}$	(48)
521	$N_2^* + H_2O \rightarrow OH + H + N_2$	$k = 4.2 * 10^{-11}$	(47)
522	$N_2^* + CO_2 \rightarrow CO + O + N_2$	$k = 1.5 * 10^{-10}$	(46)
523	$N_2^* + NO_2 \rightarrow NO + O + N_2$	$k = 1.0 * 10^{-12}$	(est.)
524	$N_2^* + SO_2 \rightarrow SO + O + N_2$	$k = 5.0 * 10^{-11}$	(8, 42)
525	$N_2^* + NH_3 \rightarrow NH_2 + H + N_2$	$k = 4.6 * 10^{-11}$	(28)
526	$N_2^* + NH_3 \rightarrow NH + H_2 + N_2$	$k = 9.0 * 10^{-11}$	(28)
527	$N_2^* + N_2O \rightarrow 2\ N_2 + O$	$k = 8.0 * 10^{-11}$	(46)
528	$N_2^* + N_2O \rightarrow N_2 + N + NO$	$k = 8.0 * 10^{-11}$	(46)
529	$N_2^* + H_2O_2 \rightarrow N_2 + 2\ OH$	$k = 2.0 * 10^{-11}$	(25)
530	$N_2^* + H_2 \rightarrow N_2 + 2\ H$	$k = 3.8 * 10^{-15}$	(28)
531	$N_2^* + N \rightarrow N_2 + N$	$k = 5.0 * 10^{-11}$	(42)
532	$N_2^* + O \rightarrow N_2 + O^*$	$k = 2.3 * 10^{-11}$	(31, 41)
533	$N_2^* + NH_2 \rightarrow N_2 + NH + H$	$k = 1.66 * 10^{-11}$	(28)
534	$N(^2D) + N_2 \rightarrow N +$ N2	$k = 9.4 * 10^{-14} * \exp(-510/T)$	(30, 44)

535	$N(^2D) + O_2 \rightarrow NO + O$	$k = 3.5 * 10^{-13} * T^{0.5}$		(30, 31, 44)
536	$N(^2D) + CO_2 \rightarrow NO + CO$	$k = 4.0 * 10^{-13}$		(30, 31)
537	$N(^2D) + NO \rightarrow N_2 + O$	$k = 7.0 * 10^{-11}$		(30)
538	$N(^2D) + NO_2 \rightarrow N_2O + O$	$k = 1.5 * 10^{-13}$		(19)
539	$N(^2D) + NO_2 \rightarrow 2\ NO$	$k = 1.1 * 10^{-13}$		(19)
540	$N(^2D) + N_2O \rightarrow N_2 + NO$	$k = 1.2 * 10^{-11} * \exp(-570/T)$		(30, 31, 44)
541	$N(^2D) + NH_3 \rightarrow NH + NH_2$	$k = 7.0 * 10^{-11}$		(40)
542	$N(^2D) + O \rightarrow N + O$	$k = 7.0 * 10^{-13}$		(75)
543	$N(^2P) + N_2 \rightarrow N2 + N$	$k = 2.0 * 10^{-18}$		(44)
544	$N(^2P) + O_2 \rightarrow NO + O$	$k = 2.0 * 10^{-12}$		(44, 75)
545	$N(^2P) + NO_2 \rightarrow N_2O + O$	$k = 1.5 * 10^{-13}$		(19)
546	$N(^2P) + NO_2 \rightarrow 2\ NO$	$k = 1.1 * 10^{-13}$		(19)
547	$N(^2P) + NH_3 \rightarrow NH + NH_2$	$k = 7.0 * 10^{-11}$		(40)
548	$N(^2P) + O \rightarrow N(^2D) + O$	$k = 1. * 10^{-11}$		(75)
549	$O_2^* + M \rightarrow O_2 + M$	$k = 5.0 * 10^{-19}$	mean value	(1)
550	$O_2^* + O_3 \rightarrow 2\ O_2 + O$	$k = 5.2 * 10^{-11} * \exp(-2840/T)$		(1)
551	$O_2^* + O \rightarrow O_2 + O^*$	$k = 1.7 * 10^{-10}$		(2)
552	$O_2^* + H \rightarrow OH + O$	$k = 1.83 * 10^{-13} * \exp(-1550/T)$		(58, 84)
553	$O_2^* + HO_2 \rightarrow OH + O + O_2$	$k = 1.66 * 10^{-10}$		(28)
554	$O_2^* + NH_2 \rightarrow HNO + OH$	$k = 1.0 * 10^{-14}$		(14, 15)

555	O_2^*	+	NH	→	NO	+	OH	$k = 1.0 * 10^{-14}$		(14, 15)
556	O_2^*	+	O^*	→	O_2	+	O	$k = 1.7 * 10^{-10}$		(2, 75)
557	$O(^1D)$			→	O	+	hν	$k = 6.3 * 10^{-3}$		(3)
558	$O(^1D)$	+	M	→	O	+	M	$k = 1.8 * 10^{-11} * \exp(+110/T)$	$(M = N_2, CO_2)$	(1, 32)
559	$O(^1D)$	+	$N_2 + M$	→	N_2O	+	M	$k = 3.5 * 10^{-37} * (300/T)^{0.6}$		(32)
560	$O(^1D)$	+	O_2	→	O	+	O_2^*	$k = 2.7 * 10^{-11} * \exp(+67/T)$		(1)
561	$O(^1D)$	+	O_2	→	O	+	02	$k = 5.0 * 10^{-12} * \exp(+67/T)$		(1)
562	$O(^1D)$	+	H_2O	→	H_2	+	O_2	$k = 2.3 * 10^{-12}$		(1)
563	$O(^1D)$	+	H_2O	→	2 OH			$k = 2.2 * 10^{-10}$		(1, 2)
564	$O(^1D)$	+	H_2O	→	H_2O	+	O	$k = 1.2 * 10^{-11}$		(1)
565	$O(^1D)$	+	NH_3	→	NH_2	+	OH	$k = 2.9 * 10^{-10}$		(32, 38)
566	$O(^1D)$	+	O_3	→	2 O	+	O_2	$k = 1.2 * 10^{-10}$		(1)
567	$O(^1D)$	+	O_3	→	2 O_2			$k = 1.2 * 10^{-10}$		(1, 60)
568	$O(^1D)$	+	H_2	→	H	+	OH	$k = 1.1 * 10^{-10}$		(1, 2)
569	$O(^1D)$	+	N_2O	→	2 NO			$k = 6.7 * 10^{-11}$		(1, 2, 32)
570	$O(^1D)$	+	N_2O	→	N_2	+	O_2	$k = 4.9 * 10^{-11}$		(1, 2, 32)
571	O^*			→	O^+	+	e^-	$k = 2.0 * 10^{-7}$		(2)
572	O^*	+	O_2	→	O_2^*	+	O	$k = 4.9 * 10^{-12} * \exp(-850/T)$		(2, 63)

573	$O^* + H_2O \rightarrow H_2O + O$	$k = 7.0 * 10^{-11}$	(64)
574	$O^* + CO_2 \rightarrow CO_2 + O$	$k = 3.0 * 10^{-11} * \exp(-1315/T)$	(63)
575	$O^* + NH_3 \rightarrow NH3 + O$	$k = 5.0 * 10^{-10}$	(64)
576	$O^* + O_3 \rightarrow 2\ O_2$	$k = 1.2 * 10^{-10}$	est., (1, 60)

Table VI. Bimolecular reactions among (ground state) neutrals

577	$OH + H \rightarrow H_2 + O$	$k = 1.38 * 10^{-14} * T * exp(-3500/T)$	(24)
578	$OH + OH \rightarrow H_2O + O$	$k = 1.0 * 10^{-11} * exp(-500/T)$	(1)
579	$H_2O + O \rightarrow 2\ OH$	$k = 2.5 * 10^{-14} * T^{1.14} * exp(-8624/T)$	(10)
580	$H_2O + H \rightarrow OH + H_2$	$k = 7.6 * 10^{-16} * T^{1.6} * exp(-9281/T)$	(10)
581	$H_2 + OH \rightarrow H_2O + H$	$k = 1.66 * 10^{-16} * T^{1.6} * exp(-1578/T)$	(10, 32)
582	$H_2 + HO_2 \rightarrow H_2O_2 + H$	$k = 1.2 * 10^{-12} * exp(-9329/T)$	(10)
583	$H_2O_2 + H \rightarrow HO_2 + H_2$	$k = 2.8 * 10^{-12} * exp(-1875/T)$	(10)
584	$H_2O_2 + O \rightarrow OH + HO_2$	$k = 1.4 * 10^{-12} * exp(-2000/T)$	(1, 32)
585	$H_2O_2 + OH \rightarrow H_2O + HO_2$	$k = 1.2 * 10^{-11} * exp(-720/T)$	(10)
586	$H_2O_2 + H \rightarrow H_2O + OH$	$k = 2.8 * 10^{-12} * exp(-1875/T)$	(10, 20)
587	$O_3 + M \rightarrow O_2 + O + M$	$k = 4.13 * 10^{-30} * T^{-1.25} * exp(-11500/T)$	(9, 10)
588	$O_3 + O \rightarrow 2\ O_2$	$k = 8.0 * 10^{-12} * exp(-2060/T)$	(32)
589	$O_3 + H \rightarrow OH + O_2$	$k = 1.4 * 10^{-10} * exp(-470/T)$	(1, 32)
590	$O_3 + HO_2 \rightarrow OH + 2\ O_2$	$k = 1.8 * 10^{-14} * exp(-680/T)$	(2, 49, 43)
591	$O_3 + OH \rightarrow HO_2 + O_2$	$k = 1.6 * 10^{-12} * exp(-1000/T)$	(1, 32)
592	$H + HO_2 \rightarrow H_2 + O_2$	$k = 3.2 * 10^{-11} * exp(-350/T)$	(1, 10, 20, 32)
593	$H + HO_2 \rightarrow 2\ OH$	$k = 3.0 * 10^{-10} * exp(-500/T)$	(1, 10, 20, 32)
594	$H + HO_2 \rightarrow H_2O + O$	$k = 9.0 * 10^{-12}$	(1, 10, 32)

595	O	+	OH	→	H	+	O_2	$k = 2.3 * 10^{-11} * \exp(+110/T)$	(1)
596	O	+	HO_2	→	OH	+	O_2	$k = 2.9 * 10^{-11} * \exp(+200/T)$	(1)
597	O_2	+	N	→	NO	+	O	$k = 4.4 * 10^{-12} * \exp(-3220/T)$	(1, 23)
598	O_2	+	HNO	→	NO_2	+	OH	$k = 1.66 * 10^{-15}$	(14, 15)
599	O_2	+	HNO	→	NO	+	HO_2	$k = 3.32 * 10^{-14}$	(14, 15)
600	O_2	+	HSO_3	→	SO_3	+	HO_2	$k = 4.00 * 10^{-13}$	(22, 29, 32)
601	O_2	+	SO	→	SO_2	+	O	$k = 2.4 * 10^{-13} * \exp(-2370/T)$	(32)
602	O_2	+	NH	→	NO	+	OH	$k = 1.26 * 10^{-13} * \exp(-764/T)$	(14, 15, 20)
603	CO_2	+	N	→	NO	+	CO	$k = 3.2 * 10^{-13} * \exp(-1711/T)$	(16)
604	NO	+	O_3	→	NO_2	+	O_2	$k = 1.8 * 10^{-12} * \exp(-1370/T)$	(1)
605	NO	+	N	→	N_2	+	O	$k = 3.25 * 10^{-11}$	(1, 32, 61)
606	NO	+	NO_3	→	2 NO_2			$k = 1.5 * 10^{-11}$	(32, 77)
607	NO	+	NO_3	→	2 NO	+	O_2	$k = 7.3 * 10^{-12} * (300/T)^{0.23} * \exp(-947/T)$	(16)
608	NO	+	HO_2	→	NO_2	+	OH	$k = 3.7 * 10^{-12} * \exp(+240/T)$	(1, 32)
609	NO	+	NH_2	→	N_2	+	H_2O	$k = 1.0 * 10^{-6} * T^{-1.96}$	est., see (20, 32)
610	NO	+	NH_2	→	N_2H	+	OH	$k = 1.0 * 10^{-12} * \exp(+330/T)$	est., see (20)
611	NO	+	NH	→	N_2	+	OH	$k = 5.15 * 10^{-11}$	(14, 15, 53)
612	NO	+	N_2H	→	N_2	+	HNO	$k = 8.3 * 10^{-11}$	(20)
613	NO	+	N_2H_2	→	N_2O	+	NH_2	$k = 5.0 * 10^{-12}$	(20)
614	NO_2	+	N	→	N_2O	+	O	$k = 3.0 * 10^{-12}$	(1)

615	NO_2 + O_3	→	NO_3 + O_2	$k = 1.2 * 10^{-13} * \exp(-2450/T)$	(1, 32, 77)
616	NO_2 + NO_3	→	NO_2 + NO + O2	$k = 2.3 * 10^{-13} * \exp(-1600/T)$	(34)
617	NO_2 + O	→	NO + O_2	$k = 5.21 * 10^{-12} * \exp(+202/T)$	(1, 50)
618	NO_2 + H	→	NO + OH	$k = 5.8 * 10^{-10} * \exp(-740/T)$	(17, 34)
619	NO_2 + OH	→	NO + HO_2	$k = 3.03 * 10^{-11} * \exp(-3400/T)$	(80)
620	NO_2 + SO	→	NO + SO_2	$k = 1.4 * 10^{-11}$	(1, 32)
621	NO_2 + SO_2	→	NO + SO_3	$k = 8.8 * 10^{-30}$	(6)
622	NO_2 + NH_2	→	N_2O + H_2O	$k = 2.2 * 10^{-12} * \exp(+650/T)$	(32)
623	NO_2 + NH	→	N_2O + OH	$k = 1.61 * 10^{-11}$	(53)
624	N_2O_4 + M	→	2 NO_2 + M	$k = 4.2 * 10^{-7} * \exp(-5550/T)$	(34)
625	N_2O_4 + H_2O	→	HNO_3 + HNO_2	$k = 1.97 * 10^{-12} * \exp(-3185/T)$	(evaluated from 85)
626	N_2O_4 + NH_3	→	HNO_3 + N_2 + H_2O	$k = 5.54 * 10^{-14} * \exp(-1410/T)$	(evaluated from 85)
627	2 HNO_2	→	NO + NO_2 + H_2O	$k = 1.0 * 10^{-20}$	(16, 70)
628	HNO_2 + O	→	NO_2 + OH	$k = 3.0 * 10^{-15}$	(72)
629	HNO_2 + OH	→	NO_2 + H_2O	$k = 1.8 * 10^{-11} * \exp(-390/T)$	(35)
630	HNO_3 + HNO_2	→	2 NO_2 + H_2O	$k = 1.6 * 10^{-17}$	(71)
631	HNO_3 + OH	→	H_2O + NO_3	$k = 4.63 * 10^{-18} * \exp(-715/T) * M + 1$ $k = 1.9 * 10^{-33} * \exp(+725/T) * M / k$ $k = k + 7.2 * 10^{-15} * \exp(+785/T)$	(32, 58)
632	HNO_3 + O	→	NO_3 + OH	$k = 3.0 * 10^{-15}$	(72)

633	$HNO_3 + H \rightarrow HNO_2 + OH$	$k = 1.0 * 10^{-13}$	(34, 56)
634	$HO_2NO_2 + O \rightarrow OH + NO_2 + O_2$	$k = 7.0 * 10^{-11} * \exp(-3370/T)$	(2, 32)
635	$HO_2NO_2 + OH \rightarrow NO_2 + H_2O + O_2$	$k = 1.3 * 10^{-12} * \exp(+380/T)$	(2)
636	$HO_2NO_2 \rightarrow HO_2 + NO_2$	$k = 3.4 * 10^{+14} * \exp(-10420/T)$	(1)
637	$N_2O + NH \rightarrow N_2 + HNO$	$k = 1.66 * 10^{-13} * T^{0.5} * \exp(-1500/T)$	(20, 24)
638	$N_2O_5 + H_2O \rightarrow 2\ HNO_3$	$k = 3.1 * 10^{-21}$	(2)
639	$NO_3 + NO_3 \rightarrow 2\ NO_2 + O_2$	$k = 7.5 * 10^{-12} * \exp(-3000/T)$	(16, 34)
640	$NO_3 + O \rightarrow NO_2 + O_2$	$k = 1.0 * 10^{-11}$	(32, 77)
641	$NO_3 + OH \rightarrow NO_2 + HO_2$	$k = 2.6 * 10^{-11}$	(86)
642	$NO_3 + HO_2 \rightarrow HNO_3 + O_2$	$k = 2.0 * 10^{-13} * \exp(+550/T)$	(37, 86)
643	$NO_3 + HO_2 \rightarrow NO_2 + OH + O_2$	$k = 8.0 * 10^{-13} * \exp(+550/T)$	(37, 86)
644	$NO_3 + CO \rightarrow NO_2 + CO_2$	$k = 1.6 * 10^{-11} * \exp(-3250/T)$	(16)
645	$SO_2 + HO_2 \rightarrow SO_3 + OH$	$k = 2.25 * 10^{-16} * \exp(+300/T)$	(32)
646	$SO_3 + H_2O \rightarrow H_2SO_4$	$k = 1.0 * 10^{-12}$	(2)
647	$SO_3 + N \rightarrow SO_2 + NO$	$k = 5.3 * 10^{-16}$	(42)
648	$HSO_3 + OH \rightarrow SO_3 + H_2O$	$k = 1.0 * 10^{-11}$	(2)
649	$SO + O_3 \rightarrow SO_2 + O_2$	$k = 3.6 * 10^{-12} * \exp(-1100/T)$	(32)
650	$SO + HO_2 \rightarrow SO_2 + OH$	$k = 9.0 * 10^{-16}$	(2)
651	$SO + OH \rightarrow SO_2 + H$	$k = 9.0 * 10^{-10} * (T/300)^{0.5}$	(26, 32)
652	$CO + OH \rightarrow CO_2 + H$	$k = 1.5 * 10^{-13} * (1 + 0.6 * P)$ P[atm]	(32)
653	$O_3 + N \rightarrow NO + O_2$	$k = 1.0 * 10^{-16}$	(1, 23)

654	$O_3 + NH_2 \rightarrow NH_2O + O_2$	$k = 2.0 * 10^{-12} * exp(-700/T)$	(74)
655	$NH_3 + OH \rightarrow NH_2 + H_2O$	$k = 8.32 * 10^{-17} * T^{1.6} * exp(-480/T)$	(76, 79)
656	$NH_3 + O \rightarrow NH_2 + OH$	$k = 1.83 * 10^{-18} * T^{2.1} * exp(-2620/T)$	(34, 79)
657	$NH_3 + H \rightarrow NH_2 + H_2$	$k = 9.1 * 10^{-15} * T^{1.3} * exp(-6570/T)$	(83)
658	$NH_2 + H_2 \rightarrow NH_3 + H$	$k = 4.15 * 10^{-12} * exp(-4420/T)$	(82, 83)
659	$NH_2 + NH_2O \rightarrow NH_3 + HNO$	$k = 8.3 * 10^{-12}$	(74)
660	$NH_2 + OH \rightarrow NH + H_2O$	$k = 7.47 * 10^{-12} * exp(-1100/T)$	(20)
661	$NH_2 + H \rightarrow NH + H_2$	$k = 1.15 * 10^{-10} * exp(-1825/T)$	(20)
662	$NH_2 + HO_2 \rightarrow NH_3 + O_2$	$k = 1.95 * 10^{-11}$	(2, 28, 82)
663	$NH_2 + HO_2 \rightarrow HNO + H_2O$	$k = 1.95 * 10^{-11}$	(82)
664	$NH_2 + HO_2 \rightarrow NH_2O + OH$	$k = 1.95 * 10^{-11}$	(est., 82)
665	$NH_2 + HNO \rightarrow NH_3 + NO$	$k = 2.0 * 10^{-10} * exp(-500/T)$	(20, 21, 51, 79)
666	$NH_2 + O \rightarrow HNO + H$	$k = 1.1 * 10^{-9} * T^{-0.5}$	(13, 20)
667	$NH_2 + O \rightarrow NH + OH$	$k = 1.2 * 10^{-11}$	(13)
668	$NH_2 + N \rightarrow N_2 + 2\ H$	$k = 1.2 * 10^{-10}$	(45, 57)
669	$2\ NH_2 + M \rightarrow N_2H_4 + M$	$k = 2.5 * 10^{-11}$ high pressure limit for $P > 250$ torr	(20, 54)
670	$2\ NH_2 \rightarrow N_2H_2 + H_2$	$k = 1.23 * 10^{-12} * exp(-1250/T)$	(51, 54, 79)
671	$NH_2 + N_2H \rightarrow N_2 + NH_3$	$k = 1.66 * 10^{-11}$	(20)
672	$NH_2 + NH \rightarrow N_2H_3$	$k = 7.2 * 10^{-11}$	(54)
673	$NH_2 + NH \rightarrow N_2H_2 + H$	$k = 6.8 * 10^{-11}$	(20, 79)

674	$NH + OH \rightarrow HNO + H$	$k = 3.3 * 10^{-11}$	(20)
675	$NH + OH \rightarrow N + H_2O$	$k = 8.3 * 10^{-13} * T^{0.5} * \exp(-1000/T)$	(20)
676	$NH + N \rightarrow N_2 + H$	$k = 1.1 * 10^{-11} * T^{0.5}$	(2, 45)
677	$NH + O \rightarrow NO + H$	$k = 3.3 * 10^{-11}$	(20)
678	$NH + O \rightarrow N + OH$	$k = 1.66 * 10^{-12} * T^{0.5} * \exp(-50/T)$	(20)
679	$2\ NH \rightarrow N_2 + H_2$	$k = 1.2 * 10^{-10}$	(54)
680	$NH + H \rightarrow N + H_2$	$k = 5.0 * 10^{-11}$	(20, 28)
681	$NH + HO_2 \rightarrow NH_2 + O_2$	$k = 7.7 * 10^{-11}$	(14, 15, 54)
682	$NH + N_2H_3 \rightarrow N_2H_2 + NH_2$	$k = 3.32 * 10^{-11}$	(20)
683	$N_2H_4 + H \rightarrow N_2H_3 + H_2$	$k = 2.2 * 10^{-11} * \exp(-1250/T)$	(2, 20, 54)
684	$N_2H_4 + O \rightarrow N_2H_3 + OH$	$k = 5.0 * 10^{-12}$	(52)
685	$N_2H_4 + O \rightarrow N_2H_2 + H_2O$	$k = 1.41 * 10^{-10} * \exp(-600/T)$	(20)
686	$N_2H_4 + NH_2 \rightarrow N_2H_3 + NH_3$	$k = 6.5 * 10^{-12} * \exp(-750/T)$	(20, 54)
687	$N_2H_4 + OH \rightarrow N_2H_3 + H_2O$	$k = 8.3 * 10^{-12} * \exp(-500/T)$	(20)
688	$N_2H_3 + H \rightarrow N_2 + 2\ H_2$	$k = 1.0 * 10^{-11}$	(2)
689	$N_2H_3 + H \rightarrow 2\ NH_2$	$k = 2.7 * 10^{-12}$	(2, 20, 54)
690	$2\ N_2H_3 \rightarrow N_2H_4 + N_2 + H_2$	$k = 6.0 * 10^{-11}$	(2)
691	$2\ N_2H_3 \rightarrow 2\ NH_3 + N_2$	$k = 1.7 * 10^{-10}$	(2, 54)
692	$N_2H_3 + O \rightarrow NH_2 + HNO$	$k = 1.66 * 10^{-11}$	(20)
693	$N_2H_3 + O \rightarrow N_2H_2 + OH$	$k = 8.3 * 10^{-12} * \exp(-2500/T)$	(20)

694	$N_2H_3 + OH \rightarrow N_2H_2 + H_2O$	$k = 1.66 * 10^{-12} * \exp(-500/T)$	(20)
695	$N_2H_2 + O \rightarrow N_2H + OH$	$k = 3.32 * 10^{-11} * \exp(-500/T)$	(20)
696	$N_2H_2 + O \rightarrow NO + NH_2$	$k = 1.66 * 10^{-11}$	(20)
697	$N_2H_2 + OH \rightarrow N_2H + H_2O$	$k = 1.66 * 10^{-11} * \exp(-500/T)$	(20)
698	$N_2H_2 + H \rightarrow N_2H + H_2$	$k = 8.30 * 10^{-11} * \exp(-500/T)$	(20)
699	$N_2H_2 + NH \rightarrow N_2H + NH_2$	$k = 1.66 * 10^{-11} * \exp(-500/T)$	(20)
700	$N_2H_2 + NH_2 \rightarrow N_2H + NH_3$	$k = 1.66 * 10^{-11} * \exp(-500/T)$	(20)
701	$N_2H + H \rightarrow N_2 + H_2$	$k = 6.14 * 10^{-11} * \exp(-1500/T)$	(20)
702	$N_2H + OH \rightarrow N_2 + H_2O$	$k = 5.0 * 10^{-11}$	(20)
703	$N_2H + O \rightarrow N_2 + OH$	$k = 1.66 * 10^{-11} * \exp(-2500/T)$	(20)
704	$N_2H + O \rightarrow N_2O + H$	$k = 1.66 * 10^{-11} * \exp(-1500/T)$	(20)
705	$HNO + H \rightarrow H_2 + NO$	$k = 9.0 * 10^{-12}$	(8, 20)
706	$HNO + H \rightarrow NH + OH$	$k = 3.0 * 10^{-20}$	(14, 15)
707	$HNO + OH \rightarrow H_2O + NO$	$k = 6.0 * 10^{-11}$	(14, 15, 20)
708	$HNO + O_3 \rightarrow NO + OH + O_2$	$k = 3.3 * 10^{-14}$	(74)
709	$HNO + O \rightarrow NO + OH$	$k = 1.66 * 10^{-13}$	(20)
710	$2\ HNO \rightarrow H_2O + N_2O$	$k = 6.56 * 10^{-12} * \exp(-2500/T)$	(20)
711	$NH_2O + O_3 \rightarrow NH_2 + 2\ O_2$	$k = 1.5 * 10^{-14}$	(74)
712	$NH_2O + O_2 \rightarrow HNO + HO_2$	$k = 2.7 * 10^{-18}$	(2)
713	$N + OH \rightarrow NO + H$	$k = 5.8 * 10^{-11}$	(1, 34)
714	$N + HO_2 \rightarrow NO + OH$	$k = 2.2 * 10^{-11}$	(33)

Table VII. Termolecular reactions

715	$O_2 + O + M \rightarrow O_3 + M$	$k_0 = 6.0 * 10^{-34} * (300/T)^{2.3}$		(1, 11, 12)
		$k_\infty = 2.8 * 10^{-12}$, $F_c = exp(-T/696)$		
716	$O_2 + H + M \rightarrow HO_2 + M$	$k_0 = 5.9 * 10^{-32} * (300/T)$		(1)
		$k_\infty = 7.5 * 10^{-11} * (T/300)^{0.5}$, $F_c = exp(-T/498)$		
717	$NO + O + M \rightarrow NO_2 + M$	$k_0 = 1.0 * 10^{-31} * (300/T)^{1.6}$		(1)
		$k_\infty = 3.0 * 10^{-11} * (T/300)^{0.3}$, $F_c = exp(-T/1850)$		
718	$NO + OH + M \rightarrow HNO_2 + M$	$k_0 = 7.4 * 10^{-31} * (300/T)^{2.6}$		(1)
		$k_\infty = 1.0 * 10^{-11}$, $F_c = exp(-T/1300)$		
719	$NO + H + M \rightarrow HNO + M$	$k = 1.0 * 10^{-32} * exp(+300/T)$		(8, 34)
720	$2\ NO_2 + M \rightarrow N_2O_4 + M$	$k = 4.7 * 10^{-35} * exp(+860/T)$	corrected for K_p	(34)
721	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	$k_0 = 3.7 * 10^{-30} * (300/T)^{4.1}$		(1)
		$k_\infty = 1.6 * 10^{-12} * (T/300)^{0.2}$, $F_c = exp(-T/280)$		
722	$NO_2 + O + M \rightarrow NO_3 + M$	$k_0 = 9.0 * 10^{-32} * (300/T)^{2.0}$		(16, 32)
		$k_\infty = 2.2 * 10^{-11}$, $F_c = 1.7782 * 10^{-2}$		
723	$NO_2 + OH + M \rightarrow HNO_3 + M$	$k_0 = 2.6 * 10^{-30} * (300/T)^{2.9}$		(1)
		$k_\infty = 5.2 * 10^{-11}$, $F_c = exp(-T/353)$		
724	$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$	$k_0 = 2.3 * 10^{-31} * (3000/T)^{4.6}$		(1)
		$k_\infty = 4.2 * 10^{-12} * (T/300)^{0.2}$, $F_c = exp(-T/517)$		
725	$N_2O_5 + M \rightarrow NO_2 + NO_3$	$k_0 = 2.2 * 10^{-3} * (300/T)^{4.4} * exp(-11080/T)$		(1)
		$k_\infty = 9.7 * 10^{+14} * (T/300)^{0.1} * exp(-11080/T)$, $F_c = exp(-T/280)$		

726	$SO_2 + OH + M \rightarrow HSO_3 + M$	$k_0 = 5.0 * 10^{-31} * (300/T)^{3.3}$		(1, 32)
		$k_\infty = 2.0 * 10^{-12}$, $F_c = exp(-T/380)$		
727	$SO_2 + O + M \rightarrow SO_3$	$k = 4.0 * 10^{-32} * exp(-1000/T)$		(1)
728	$SO_3 + O + M \rightarrow SO_2 + O_2$	$k = 8.1 * 10^{-30}$		(1)
729	$CO + O + M \rightarrow CO_2 + M$	$k = 6.6 * 10^{-33} * exp(-2173/T)$		(10)
730	$O + O + M \rightarrow O_2 + M$	$k = 2.76 * 10^{-31} / T$	k_0 is used	(10)
731	$H + H + M \rightarrow H_2 + M$	$k = 2.67 * 10^{-31} * T^{0.6}$	k_0 is used	(10)
732	$OH + H + M \rightarrow H_2O + M$	$k = 1.1 * 10^{-23} * T^{-2.6}$		(10)
733	$2\ OH + M \rightarrow H_2O_2 + M$	$k_0 = 6.9 * 10^{-31} * (300/T)^{0.8}$		(1)
		$k_\infty = 3.0 * 10^{-11}$, $F_c = exp(-T/913)$		
734	$OH + HO_2\ (+ M) \rightarrow H_2O + O_2\ (+ M)$	$k = 4.8 * 10^{-11} * exp(+250/T)$		(1, 32)
735	$2\ HO_2\ (+ M) \rightarrow H_2O_2 + O_2\ (+ M)$	$k = 2.2 * 10^{-13} * exp(+600/T)$		(1, 32)
		$+ 1.9 * 10^{-33} * (M - [H_2O]) * exp(+980/T)$		
		$k = k * (1 + 1.4 * 10^{-21} * exp(+2200/T) * [H_2O])$		
736	$N + N + M \rightarrow N_2 + M$	$k = 8.3 * 10^{-34} * exp(+500/T)$	k_0 is used	(34)
737	$N + O + M \rightarrow NO + M$	$k = 1.8 * 10^{-31} * T^{-0.5}$		(34)
738	$NH_2 + H + M \rightarrow NH_3 + M$	$k = 6.0 * 10^{-30}$		(2, 82)
739	$NH + H + M \rightarrow NH_2 + M$	$k = 5.5 * 10^{-32} * T^{-0.5}$		(20)

Table VIII. Particle formation and heterogeneous reactions

$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$	(see text)
$NH_3 + NH_4HSO_4 \rightarrow (NH_4)_2SO_4$	(see text)
$NH_3 + HNO_3 \rightarrow NH_4NO_3$	(see text)
$HNO_2 + \text{particle} \rightarrow 1/3\ HNO_3 + 2/3\ NO + 1/3\ H_2O$	$\alpha = 0.1$
$HNO_2 + \text{particle} \rightarrow 0.5\ NO + 0.5\ NO_2 + 0.5\ H_2O$	$\alpha = 0.01$
$HNO_2 + \text{particle} \rightarrow NO + 0.5\ H_2O + 0.25\ O_2$	$\alpha = 1.0 * 10^{-4}$
$HNO_2 + NH_3 + \text{particle} \rightarrow N_2 + 2\ H_2O$	$\alpha = 0.0$
$2\ HNO_2 + SO_2 + \text{particle} \rightarrow 2\ NO + H_2SO_4$	$\alpha = 1.0 * 10^{-5}$
$HNO_2 + HNO_3 + \text{particle} \rightarrow 2\ NO_2 + H_2O$	$\alpha = 1.0 * 10^{-4}$
$HNO_3 + \text{particle} \rightarrow 0.5\ NO_2 + 0.5\ NO_3 + 0.5\ H_2O$	$\alpha = 1.0 * 10^{-4}$
$HNO_3 + \text{particle} \rightarrow NO_2 + 0.5\ H_2O + 0.25\ O_2$	$\alpha = 1.0 * 10^{-4}$
$2\ HNO_3 + SO_2 + \text{particle} \rightarrow 2\ NO + H_2SO_4 + O_2$	$\alpha = 3.0 * 10^{-3}$

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