

Basic ion reactions and kinetics in plasmas

W. Lindinger

Institut für Experimentalphysik, Karl Schönherrstr. 3,
A 6020 Innsbruck, Austria

Abstract - Data collected over the past years on ion neutral interactions have revealed generalizations for classes of interactions, such as charge transfer, proton transfer, reactions with rearrangements of bonds, energy transfer, isotope exchange and associative reactions. These are discussed below as well as some of the applications.

INTRODUCTION

The formation of charged particles within a neutral gas volume leads to the creation of a plasma, having quite distinct properties, both macroscopic (total charge carrier density, temperature, etc.) and microscopic ones (types of ions and their internal excitations) depending on the original neutral gas constituents. Electron impact on neutrals and photoionization are producing ions, at the same time destroying or dissociating the originally present neutral molecules. Primary ions, partly excited, partly in their ground states, undergo a variety of reactive and/or nonreactive collisions with neutrals thereby either changing their state of excitation or even their identity. In ion molecule reactions, the formation of new chemical bonds may occur, thus creating new neutral molecules, which are even more complex than the original neutral gas constituents. Plasma deposition of organic films and the formation of complex molecules in interstellar clouds are examples of molecular synthesis in plasmas. In ionized gases usually tens or even hundreds of ion neutral reactions proceed simultaneously. In order to unravel these patterns of reactions, experimental methods, such as the selected ion flow (drift) tube (SIF(D)T) have been developed, providing information on the reactivities as dependent on the kinetic and internal energy of the reactants, but also on the excitation and deexcitation of ions in collisions with neutrals involving molecular energy transfer.

EXPERIMENTAL

The interactions between ions and neutrals at energies higher than a few eV are usually investigated by means of beam experiments (ref. 1-3). A beam of monoenergetic ions, A^+ , with a total initial current $i(A^+)_0$ passes through a collision chamber, containing the neutral target gas B at a number density $[B]$. On its way L through the collision chamber the ion beam suffers losses due to collisions between A^+ and B leading to an attenuation of the ion current in the form

$$i(A^+)_L = i(A^+)_0 e^{-[B] \cdot \sigma \cdot L}, \quad (1)$$

where σ is the total cross section for the interaction process. At thermal

energies and even up to ~ 1 eV it becomes extremely difficult to produce monoenergetic ion beams and thus only a few beam experiments operate in this low energy regime (ref 4-8). However, this regime is the most important one for ion/neutral reactions occurring in natural and technical plasmas, which cover temperatures as low as a few tens of Kelvin (K), as in the case of interstellar dense and diffusive clouds, up to several thousand K, e.g. in the ionospheres of planets or in gaseous discharges.

In order to investigate Ion-Neutral-Reactions in the low energy (thermal) regime a wide variety of so called swarm experiments have been developed over the past three decades, such as the Stationary (ref. 9,10) and Flowing (ref. 11,12) Afterglows or Drift Tubes (ref. 13-15).

In a swarm experiment, the reactant ions, A^+ , are introduced into a chamber or tube filled with a nonreactive buffer gas, such as He or Ar (Fig. 1). The ions undergo many collisions with the buffer gas and reach some kind of equilibrium velocity distribution, which they retain as long as they stay in the chamber. If we now add traces of reactant gas B to the buffer gas, after many collisions with the buffer gas particles, an ion A^+ will undergo a potentially reactive collision with an atom or molecule B:

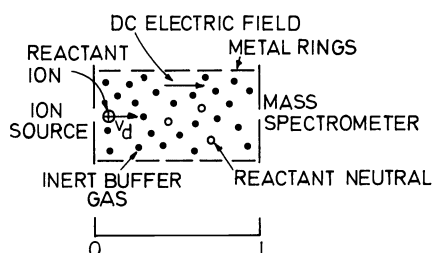


Fig. 1. Schematic representation of a drift tube

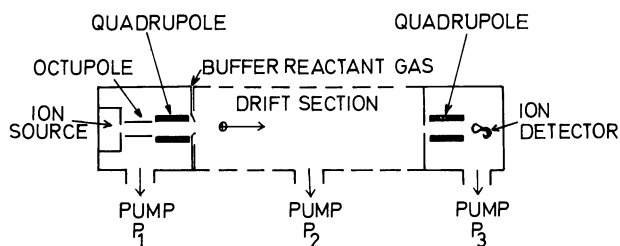


Fig. 2. Selected Ion Flow Drift Tube (SIFDT) with Octupole-ion-preparation section.



and as a function of the density $[B]$, a decline of the ion signal monitored in a detection system is observed according to

$$[A^+] = [A^+]_0 e^{-[B]k \frac{L}{v}} \quad (3)$$

where k is the reaction rate coefficient.

In modern swarm experiments, (ref. 16,17) such as the Selected Ion Flow Drift Tube (Fig. 2), a variable homogeneous electric field applied to the reaction chamber allows for the controlled variation of the mean kinetic energy, KE_{ion} of the reactant ions, drifting in the buffer gas, from which the mean kinetic energy between the reactant ions and reactant neutrals embedded in the buffer gas, KE_{cm} can be obtained according to (ref.15,18-22)

$$KE_{cm} = \frac{M(m+M_{ion})}{2(M+M_{ion})} v_d^2 + \frac{3}{2} k_B T \quad (4)$$

where M , m and M_{ion} are the masses of the reactant neutrals (B) of the buffer gas and of the reactant ions respectively, and v_d is the drift velocity of the reactant ions in the buffer gas.

It is now common that rate coefficients obtained in drift tube experiments are expressed as a function of KE_{cm} , derived using Equ. (4).

A fraction of the ions produced in an ion source may be in long-lived excited vibrational or electronic states. In many cases, ions retain this excitation even on their way through the drift chamber, surviving many collisions, especially when He is used as the buffer gas, and when E/N is kept low (ref. 23-25). On the other hand, heavier buffer gases, such as Ne, Ar, or Kr are more efficient in quenching ionic excitation, but at the same time ions entering the drift chamber in their ground state may become vibrationally excited (ref. 26-31), reaching an equilibrium distribution (when the drift tube is long enough) that depends on E/N . At high E/N this equilibrium also can be reached in a He buffer. According to calculations of Viehland et al. (ref. 32-35), for molecular ions drifting in an inert buffer gas, the effective internal temperature T_{eff} attained by the ions is given by the relation

$$\frac{3}{2} k_b T_{eff} = \left[1 + \frac{m_B}{M_{ion}} \xi \right] \left(\frac{3}{2} k_b T + \frac{1}{2} m v_d^2 \right) (1+\beta). \quad (5)$$

β is a small correction term ($\beta \ll 1$), and ξ is a dimensionless ratio of collision integrals that characterizes the fractional energy loss due to inelastic collisions.

That in fact at elevated E/N even He becomes quite efficient for quenching and creating of vibrational excitation of molecular ions has been demonstrated experimentally (ref. 36). It becomes important, where the ion-buffer collision energy is comparable to or even exceeds vibrational spacings in molecular ions. Quenching efficiency and vibrational excitation efficiency are related by the principle of microscopic reversability. Fig. 3 represents measured vibrational temperatures of N_2^+ in He as a function of E/N .

Which kind of data then do we need in order to elucidate the ion chemistry occurring in plasmas ?

In typical technical plasmas E/N can have substantial values, thus the kinetic energy KE_{cm} between the ions and their collision partners is not in equilibrium with the temperature of the neutral gas (buffer gas) they are drifting in. We thus need rate coefficient data as a function of KE_{cm} . Depending on the kind of buffer gas, the internal (vibrational) temperature, T_{eff} , of molecular reactant ions changes.

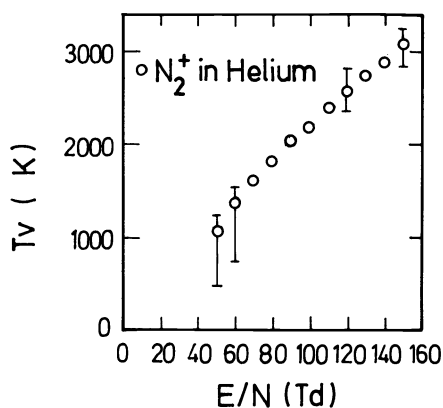
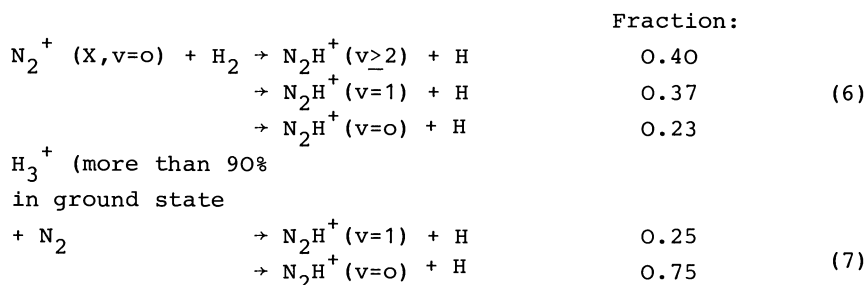


Fig. 3. Vibrational temperature of N_2^+ drifting in a helium buffer gas.

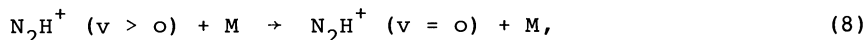
Experiments performed in the proper buffer gases allow to obtain rate coefficients as dependent on KE_{cm} and on T_{eff} .

A widely neglected point however is that in ion molecule reactions, product ions usually are not produced in their ground state but rather vibrationally and often also electronically excited. Excited ions however may have strongly different reactivities compared to ground state ions, It is thus necessary to investigate the nascent state distributions of ions depending on the processes creating them and in addition to measure rate coefficients for reactive and quenching collisions for the ions in their respective excited states. A drastic example (ref. 37) is the production of N_2H^+ in the two reactions (6) and (7)



The reaction of N_2^+ with H₂ producing N_2H^+ has an exothermicity of ~ 2 eV, while the proton transfer from H_3^+ to H₂ is exothermic only by 0.5 eV. The high fraction of excited $N_2H^+(v)$ in reaction (6) compared to the one in reaction (7) reflects qualitatively this difference between the exothermicities. While $N_2H^+(v \geq 2)$ undergoes fast proton transfer with Argon, $N_2H^+(v < 1)$ does not, thus in a plasma containing Ar the further reactive sequences involving N_2H^+ will be quite different, depending on the process in which N_2H^+ is formed.

The combination of an ion source (electron impact or discharge type source) and an octupole storage section followed by a quadrupole analyzer as shown in Fig. 2 allows to introduce ions into the drift region of a SIFDT retaining closely their nascent state distribution. How this is achieved can best be demonstrated using the above mentioned reactions (6) and (7). $N_2^+(v=0)$ originating from a high pressure ion source is introduced into the octupole, where a small fraction (~ 1%) is allowed to collide with H₂. The product ions N_2H^+ are then mass selected before having the chance to undergo further collisions with any neutrals M which could result in the quenching process



and are then introduced via a Venturi type inlet into the He buffer in the drift section. As He does not significantly quench the vibrational excitation of N_2H^+ at low E/N, the addition of Kr and Ar respectively as reactants into the drift section causes the fast conversion of $N_2H^+(v \geq 1)$ into KrH^+ and of $N_2H^+(v \geq 2)$ into ArH^+ , thus allowing us to obtain the fractions of $N_2H^+(v \geq 2)$, $N_2H^+(v=1)$ and $N_2H^+(v=0)$. Similarly in the case of reaction (7), H_3^+ from the high pressure electron impact source is introduced into the octupole, where traces of N₂ allow for the conversion of small fractions of H_3^+ into N_2H^+ which is then analyzed in the same way as mentioned above.

RESULTS

In view of these aspects recent data on several types of ion-neutral-interactions will be discussed in the following.

Binary collisions

Due to the attractive potential of the ion-induced dipole interaction "capture" of the reactant ion and the neutral collision partner into an orbiting complex takes place with a rate

$$k_L = 2\pi e \left(\frac{\alpha}{m_r} \right)^{1/2}, \quad (9)$$

usually called the Langevin limiting rate (ref. 38,39). α is the polarizability of the neutral and m_r the reduced mass between the collision partners. Additional factors, reaching the same order of magnitude as k_L need to be added, when permanent dipoles or quadrupoles exist (ref. 40-42) in the neutral reactant (the respective values usually are indicated as k_{ADO} , k_{AADO} , and in the following the symbol k_C is used for all of these theoretical limits).

Experiments have shown that in many cases, even whole classes of ion neutral reactions proceed with rate coefficients as fast as k_C (typically $\sim 1 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$), i.e. each capture into an orbiting complex leads to a reaction. Reactions proceeding with rates $k \sim k_C$ retain this fast reactivity (ref. 24) independently on KE_{cm} in the range from thermal energies up to a few eV. However rate coefficients, which are much smaller than k_C usually show strong energy dependences.

Charge transfer processes between atomic ions and molecular neutrals tend to be fast (ref. 43) when the molecular ground state and the molecular ionic state corresponding to a resonant charge transfer are connected by large Franck-Condon-Factors ($> 10^{-5}$). Despite the existence of large FCF's however, these charge transfers frequently do not proceed via resonant energy levels as has been shown for the fast reactions of He^+ with O_2 , Ar^+ with H_2O and $\text{O}^+(^2D)$ with N_2 and O_2 (ref. 44-47) respectively. Small FCF's do not seem to allow for a fast charge transfer to occur. These slow charge transfer processes exhibit strong energy dependences, often reflecting the access into favourable, but endoergic product channels at elevated KE_{cm} . This has been shown e.g. for $\text{Ar}^+ + \text{O}_2$ (Fig. 4), where above a few tenths of an eV, the slightly endoergic product channel

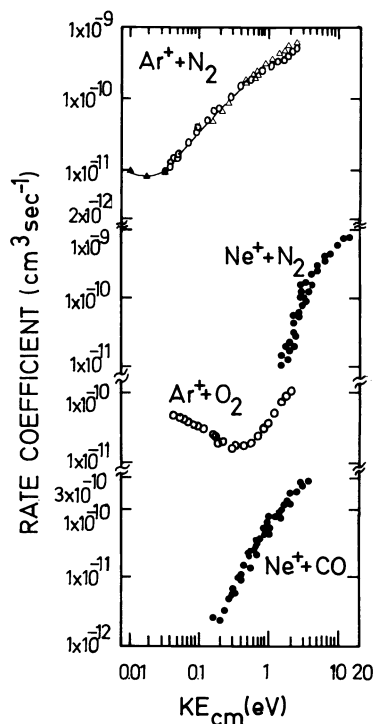
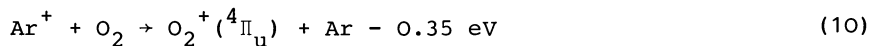


Fig. 4. Rate coefficients, k , as a function on KE_{cm} for several charge transfer reactions.



is populated.

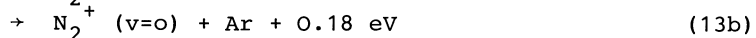
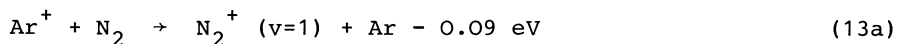
The rate coefficient for Ne^+ reacting with CO increases towards large values (k close to k_c) at $\text{KE}_{\text{cm}} \gtrsim 1 \text{ eV}$ and at the same time the endoergic dissociative charge transfer channel (11b) becomes dominant,



Adding kinetic energy also allows the reaction of Ne^+ with N_2 to proceed via the favourable, highly predissociative $\text{N}_2^+ (\text{C}_u^+)$ state, resulting in reaction channel (12b) at energies $\text{KE}_{\text{cm}} \geq 3 \text{ eV}$ (ref. 50,51).



The most thoroughly studied charge transfer between an atomic ion and a molecular reactant (both experimentally and theoretically) is the one of Ar^+ with N_2 , (ref. 52-56) which proceeds via the slightly endoergic channel (13a)



at energies above room temperature, and only at very low temperatures where "rotational trapping" occurs, is the exoergic product channel (13b) into $\text{N}_2^+ (v=0)$ populated at a significant rate.

Proton transfer reactions play a dominant role in practically any system involving hydrocarbons (ref. 57,58). Neutral atoms and molecules possess proton affinities, PA, and therefore if PY (Y) is significantly larger than PA(X), the reaction



is exothermic. All significantly exothermic proton transfer reactions are fast and proceed with rate coefficients close to k_c with slight variations depending on the exothermicity of the reactions, as was shown by Bohme (ref. 98). Proton affinities have been obtained for hundreds of neutral species (ref. 59) usually by measuring the concentrations, XH^+ and YH^+ under conditions, where the forward and back reactions (15)



are in equilibrium, thus yielding the equilibrium constants K according to

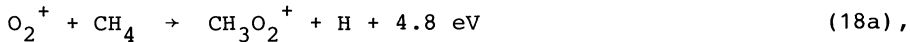
$$\frac{[\text{YH}^+][\text{X}]}{[\text{XH}^+][\text{Y}]} = \frac{k_f}{k_r} = K. \quad (16)$$

Values of K obtained at different temperatures in temperature variable Selected Ion Flow Tubes, or in special cases obtained in Drift Tubes are then plotted in the form of Vant Hoff diagrams, according to

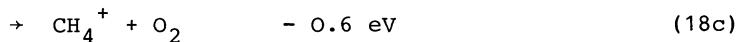
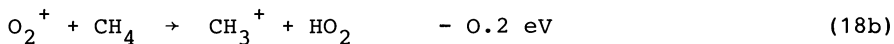
$$RT \ln K = \Delta H^{\circ} - T\Delta S^{\circ} \quad (17)$$

from which both ΔS and ΔH are obtained. ΔH is by definition the difference in the proton affinities.

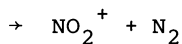
Reactions with rearrangements of bonds have thermal rate coefficients often being considerably smaller than k_c indicating that the lifetime of orbiting complexes is not long enough to allow for the bond rearrangements to occur with high efficiency. A typical example is the reaction (ref. 24,25,27,60)



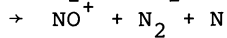
which proceeds at a very slow rate ($k = 6 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$) at room temperature. Only when KE_{cm} is increased high enough, so that the slightly endoergic channels



involving no complicated bond rearrangements, become energetically accessible, does the rate coefficient of the reaction increase dramatically. Also the reactions (ref. 61)



and



require rearrangements of bonds and thus have rate coefficients which are small at room temperature showing strong changes as a function of KE_{cm} .

Energy transfer processes, such as the vibrational relaxation of N_2^+ ($v=1$) by Ne, N_2 , O_2 and CO_2 (ref. 62) and by Kr and NO (ref. 63) or the relaxation of O_2^+ ($v = 1$ and $v = 2$) by various neutrals have been investigated using swarm experimentals (ref. 64) and most recently results were obtained in Innsbruck (ref. 65,66) on the quenching rate coefficients, k_q , of NO^+ ($v = 3$ and 1) for various collision partners. Coupling between the NO^+ -vibration and the NO^+ -neutral vibrational modes, enables NO^+ vibrational energy to be transferred to the neutral collision partner. This in turn leaves the complex with enhanced translational energy. This coupling is stronger, the higher the dissociation energy of the bound ion-neutral complex is. The latter is proportional to the polarizability of the neutral (in a first order approximation) and thus an increase of k_q with increasing α of the neutral collision partner is observed. A detailed model on the quenching of ionic vibration has been developed recently by Ferguson, showing the strong correlation between association and quenching reactions of ion-neutral pairs (ref. 23).

Isotopic exchange reactions are of special interest in high pressure, but also in low temperature plasmas. Reactions of the type



are exoergic because of the lower zero point energy of the heavier molecule C^{18}O as compared to the one of C^{16}O . Detailed investigations of Smith and his group (ref. 67-69) indicate that many of the isotopic abundances observed in interstellar molecules, which differ from the respective abundances present in terrestrial molecules, can be understood on the basis of isotopic enrichment resulting from exchange reactions at low temperatures.

Associative reactions.

The lifetimes τ , of typical complexes formed in collisions between ions and neutrals at room temperature lie below 10^{-9} sec. Therefore association reactions involving stabilizing collisions by a third partner do not play a significant role in hot, low density plasmas. Specific ions, such as CH_3^+ , however, form much longer-lived complexes with values $\tau > 10^{-6}$ sec even at room temperature, so that their associations can compete with binary reactions even at low pressures. Moreover when τ becomes very large (e.g., at low temperature) stabilization of the complex may occur by the emission of an infrared photon and collisions with a third body are no longer required for association to occur. Thus at interstellar conditions association reactions are important even though densities are extremely low. Rate coefficients for association reactions show the typical strong temperature dependences of T^{-u} , (ref. 68) with u being in the range from 2.7 to 4.4.

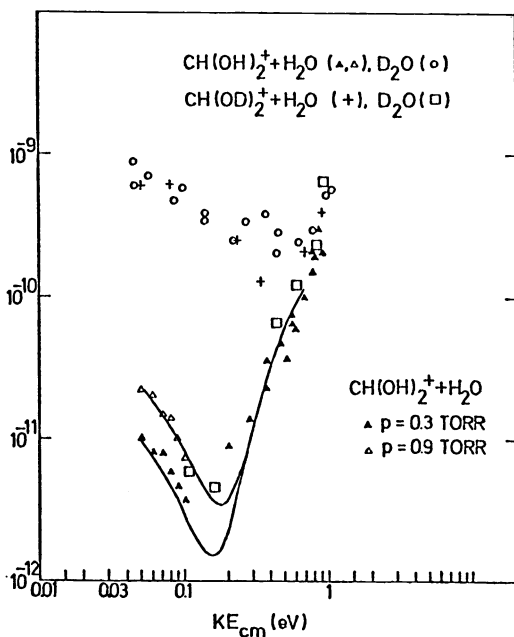
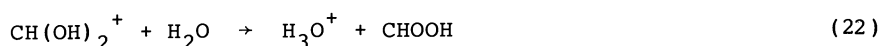


Fig. 5. Rate coefficients for the reaction of protonated formic acid (and its deuterated form $\text{CH}(\text{OD})_2^+$) with H_2O and D_2O .

The absolute values of k vary strongly from one reaction partner to the other but correlate strongly with the complex binding energies, e.g. $D(\text{CH}_3^+ \cdot \text{CO}) > D(\text{CH}_3^+ \cdot \text{O}_2)$. An interesting reaction system is protonated formic acid and H_2O together with its deuterated analogues, and rate coefficients for this system are shown in Fig. 5. $\text{CH}(\text{OH})_2^+$ undergoes fast isotopic exchange with D_2O and it associates strongly with H_2O at low KE_{cm} (< 0.1 eV), while the increase of the rate coefficient between 0.2 and 1 eV reflects the endoergic proton transfer



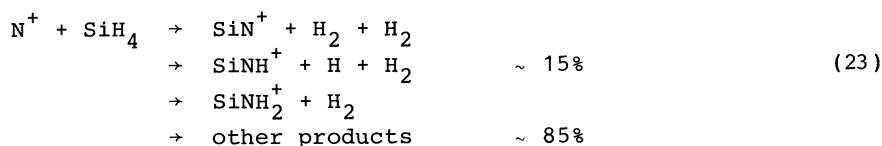
APPLICATIONS

Ionospheric plasma: The ion chemistry of the earth's ionosphere has been the subject of intensive investigation for more than a decade, starting in 1966 and is understood by now in great detail owing to the vast amount of laboratory data produced by the NOAA group of Ferguson (ref. 70).

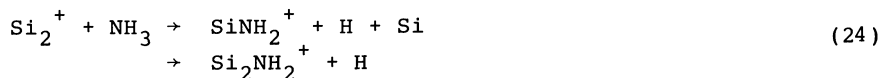
Interstellar clouds: Over the past few years research astronomers have detected a variety of neutral molecules in interstellar clouds. Considerable amounts of H_2O , NH_3 and CH_4 are present in nearly all types of dark and dense clouds, and with lower densities various acids, alcohols, aldehydes and ethers are present. Under the unfavorable conditions present in interstellar media (low T and low density) neutral chemistry cannot be responsible for the buildup of these neutrals.

Smith and his group at Birmingham (ref. 71) have shown in a number of laboratory experiments how, many of the detected neutrals are produced in ion molecule reactions followed by dissociative recombinations. Most recently we have performed investigations on reactions between ions and atomic hydrogen (ref. 72,73) as well as atomic nitrogen, which play an important role in the synthesis of interstellar molecules.

Plasma etching and plasma deposition: Investigations of etch plasmas have shown that the simultaneous impact of both, ions and neutral radicals is favouring high etch rates connected with highly anisotropic etching, however ion-molecule reactions only seem to be of importance in etch plasmas as far as they contribute to the production of neutral radicals. On the other hand molecular synthesis occurring in deposition plasmas may be strongly influenced by ion-neutral-reactions. E.g. Si_3N_4 is formed in plasmas containing SiH_4 and NH_3 . Recent investigations have shown, that the steps for formation of Si-N bonds include reactions such as (ref. 74)



and



However, while the ion chemistry of plasmas like the ionosphere is well understood, only a first step has been done for the investigation of the reaction kinetics of deposition plasmas.

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