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A Comprehensive Database on Air Plasma Kinetics

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INTRODUCTION

Plasma is frequently termed “the fourth state of matter” besides solid, liquid and gas. This is because, just like a liquid which boils when sufficient energy is provided and change into gas. Similarly, when a gas is heated will create a plasma which is a mixture of positively charged particles (ions) and negatively charged particles (electrons).

Plasma is a state of matter that is frequently composed of as a subset of gases, but the two states perform very contrarily. Similar to gases, plasmas do not have fixed shape or volume and are comparatively less compact than solids and liquids. Differently from conventional gases, plasmas are formed of atoms in which some or all of the electrons broke free from the parent nuclei, forming ion-electron pairs.

It is so hot that the electrons are torn away from the atoms making an ionized gas. It encompasses of more than 99% of the perceptible universe. During night, the plasma in the sky sparks in the form of stars, nebulas and also the auroras that occasionally undulate above the north and south poles.

As considerable part of the world is formed of plasma, its manners and properties are of deep curiosity to researchers in different areas. As Plasmas are formed of charged particles so they might have a net charge of zero above their whole volume but not at the level of single particles. This shows that the electrostatic forces amongst the particles in the plasma develop substantially along with the effect of magnetic fields. Significantly, at the temperatures which is mandatory for the objectives of applied fusion energy, all substances are in the arrangement of plasma. Scientists make usage of the properties of plasma as a charged gas to restrain it through magnetic fields and to raise the temperatures greater than the core of the sun. As the plasma is formed of charged particles, plasmas are able to perform things that gases cannot do like conduct electricity. Moreover, as moving charges create magnetic fields so plasmas also can devise them.

Scientists study plasmas for the production of computer components like chips, rocket impulsion devices, cleaning the environment, terminating biological dangers, curing wounds and added thrilling applications.

They can do so at far-off places as compared to an ordinary gas. Hence, the waves develop more significant when talk over what drives are carried on in a plasma. Alfvén wave is the example of one such wave and it has been named after a Swedish Nobel laureate Hannes Alfvén who was a physicist. An Alfvén wave occurs after the magnetic field inside a plasma is troubled. This creates a wave that moves alongside the field lines. There is certainly not an actual equivalent to this in conventional gases. There might be a possibility that Alfvén waves are the cause for the temperature of the solar corona which is also a plasma

One more specific feature of plasmas is that they can be detained in position by magnetic fields. Furthermost fusion power study is focused on creating the conditions for fusion and one of the most important needs is very hot plasma — at millions of degrees. As no physical substance can enclose it, so researchers and engineers have rotated to magnetic fields for the job.

1.1 Definition of Plasma

When the temperature of a solid substance is increased, its condition modifies from solid to liquid and follows into gas. When the temperature is further increased from a given level, it passes into a state where the thermal energy of its component particle is so abundant that the electrostatic forces which generally binds electrons to atomic nuclei are overcome. Instead of hot gas composed of electrically neutral atoms, we then have a mixed population of charged and neutral particles. With increasing temperature, the number of ionized particles increases, and the ionized gas starts behaving differently. After the fraction of ionized particles is sufficiently high the ionized gas starts exhibiting the collective behaviour and the state of matter is plasma, and it is neither solid nor liquid nor gas. Plasma is thus defined as a quasineutral gas of charge and neutral particles which exhibits collective behaviour. Quasineutrality of plasma implies that the electron density n_e is nearly equal to the ion density n_i so that $n_i \approx n_e \approx n$, where n is the number density of plasma particles called the plasma density; but the plasma is not so neutral that all the interesting electromagnetic phenomena vanish. The collective behaviour implies that the motion of species depends not only on the local conditions but also on the state of the plasma far away from the point of interest. The word “plasma” is deriving from Greek and means something moulded or fabricated. The existence of “the fourth state of matter” was first identified by Sir William Crookes in 1879, however, the term plasma was introduced by I. Langmuir in 1928 to describe the state of matter in the positive column of glow discharge tube. Plasma is thus an ionized gas, satisfying certain criteria to be discussed in next Sections; however, any ionized gas cannot be called plasma.

1.2 APPLICATIONS OF PLASMA

Because of its diverse nature plasma finds application in various fields such controlled thermonuclear fusion, surface treatment, biomedical applications, lighting, medicine, electronics, transportation and space propulsion, display technology, space physics, solid state plasma, gas lasers, etc. Some of the important and interesting applications of plasma in various fields are discussed here.

Non-equilibrium is one of the important features of an atmospheric gas discharge plasma. It involves complicated physical-chemical processes and plays a key role in various actual plasma processing. In this report, a novel complete non-equilibrium model is developed to reveal the non-equilibrium synergistic effects for the atmospheric-pressure low-temperature plasmas (AP-LTPs). It combines a thermal chemical non-equilibrium fluid model for the quasi-neutral plasma region and a simplified sheath model for the electrode sheath region. The free-burning argon arc is selected as a model system because both the electrical-thermal-chemical equilibrium and non-equilibrium regions are involved simultaneously in this arc plasma system. The modelling results indicate for the first time that it is the strong and synergistic interactions among the mass, momentum and energy transfer processes that determine the self-consistent non-equilibrium characteristics of the AP-LTPs. An energy transfer process related to the non-uniform spatial distributions of the electron-to-heavy-particle temperature ratio has also been discovered for the first time. It has a significant influence for self-consistently predicting the transition region between the “hot” and “cold” equilibrium regions of an AP-LTP system. The modelling results would provide an instructive guidance for predicting and possibly controlling the non-equilibrium particle-energy transportation process in various AP-LTPs in future. Atmospheric-pressure low-temperature plasma (AP-LTP) operates in a non-equilibrium state under most operating conditions. One of the major features of AP-LTPs is that the characteristic electron energy ranges from a few eV to 10 eV, while the heavy-particle temperature varies from around the room temperature to a level which is comparable to but usually lower than the electron temperature. This results from the physical facts that the significant mass difference between electrons and heavy particles (e.g., molecules, atoms and their ions), and consequently, the lower energy exchange rate between the subsystems of electrons and heavy particles compared with that of power input; and the inevitable involvement of the solid walls in the production and application of the laboratory plasmas. There may exist three types of non-equilibrium in an AP-LTP system: (i) non-electrical-

equilibrium (NEQ): if a conductive or non-conductive object is inserted into the plasma region, a sheath deviating from the quasi-charge neutrality condition arises between the object surface and the plasma region^{3,4}, and most of the total electric potential drop occurs at this NEQ region. (ii) Non-local-thermodynamic-equilibrium (NLTE): the low mass ratio of electrons to heavy particles in plasmas (e.g., 10^{-5} for argon) leads to an insufficient elastic energy exchange between electrons and heavy particles; and thus, the whole plasma system will be in an NLTE state, especially if the plasma density is also not high enough. (iii) Non-local-chemical-equilibrium (NLCE): since the mean electron temperature is around several electron volts (eV), which is lower than the inelastic collision energy thresholds of tens of eV, the excitation and ionization rates decrease significantly particularly when interacting with cold gas; and thus, the plasma will be in an NLCE state. The non-equilibrium of the AP-LTPs is of great importance because we can re-distribute the input energy to other types of energies at various freedoms for their wide applications, e.g., kinetic energy in plasma flow control, electronically and vibrational excited energies in plasma assisted combustion, energies stored in various reactive species with optimized non-chemical equilibrium spatial distributions in plasma-aided synthesis of Nanoscale materials^{7–12}, etc. However, it is so difficult to describe, explain, and use such non-equilibrium in the AP-LTPs since three types of non-equilibrium usually appear in the same discharge. Even worse, there may co-exist the equilibrium and three types of non-equilibrium in the same AP-LTP system, for example, the free-burning arc. Therefore, it is rather difficult to describe this strongly coupled phenomenon self-consistently. In our opinion, except for the NEQ effect in plasma sheath^{13–15}, the NLCE process plays an important role among these three types of non-equilibrium for various types of AP-LTPs with wide applications such as plasma biomedicine, advanced materials processing, plasma-assisted ignition or combustion, environmental protection, etc. This is because the chemical reactions determine not only the spatial distributions of the species number densities but also the corresponding energy transfer processes significantly. For example, in an LCE-NLTE modelling of an arc discharge by a physically incorrect increase in the elastic collision frequency between electrons and heavy particles had to be made for obtaining the close electron and heavy-particle temperature distributions in the arc fringe region. This is because the approaching of the electron and heavy-particle temperatures to each other in the arc fringe region results physically from the energy re-distribution between the subsystems of electrons and heavy species due to the chemical reactions. In recent years, although some modelling work on the NLCE plasmas have been conducted, for example, the mutual interactions between the non-equilibrium effects of NLCE and NLTE have not been completely revealed with no

considerations of the coupled energy and particle balance processes in the same plasma system. Furthermore, even purely for the NLTE situations, the spatially non-uniform temperature distributions of the electron and heavy-particle subsystems would: (i) influence the energy transfer process of the electron or heavy-particle subsystem itself through the traditional heat conduction, convection processes, and the elastic collision process between electrons and heavy particles, Q_{eh} el; (ii) result in an extra energy transfer process to the electron or heavy-particle subsystem due to the spatial gradient of the temperature ratio, the term containing $\nabla \theta \rightarrow \ln$ (here $\theta = T_e/T_h$) in the energy conservation equations of electrons and heavy particles. To our knowledge, the second non-equilibrium energy transfer process has never been reported up to now. This, to some extent, indicates a mutual influence between the electron and heavy-particle subsystems. In this study, an atmospheric free-burning argon arc plasma, is selected as a typical AP-LTP. the goal of this report is to reveal the NLTE-NLCE synergistic effects, especially the self-consistent transition between the thermal-chemical equilibrium and non-equilibrium states in the same AP-LTP system based on the self-consistent considerations of the energy and particle balance processes in plasmas This result provides a deep understanding to and a complete evaluation of the strongly coupled thermal and chemical non-equilibrium, and a constructive guidance for the possible control of the non-equilibrium particle-energy transportation process in the AP-LTPs in future.

Modelling Results

In this study, three dimensionless parameters are employed to describe the non-equilibrium features of the plasmas: (i) the temperature ratio, $\theta (=T_e/T_h)$, to quantitatively describe the NLTE state of the plasmas; (ii) the chemical reaction ratio, $\xi (=r_{ion}/r_{rec})$, and the electron number density ratio, $\zeta = * (/ n_n) e_e$, to indicate the NLCE state of the plasmas, where r_{ion} and r_{rec} are the ionization and recombination rates of the chemical reaction $Ar + e \leftrightarrow Ar^+ + 2e$, n_e and $* n_e$ represent the electron number densities based on the solution of the non-equilibrium governing equations and the Saha equation with an assumption of LCE, respectively. Therefore, the physical meanings of the preceding dimensionless parameters can be explained as: $\theta=1.0$ for the LTE state, while $\theta>1$ indicating the deviations of plasmas from the LTE state and a higher value of θ representing a higher non-thermal-equilibrium degree; similarly, $\xi=\zeta=1.0$ for the LCE state with a detailed balance of chemical reactions, and the higher or lower values than 1.0 for ξ and ζ indicating the higher non-chemical-equilibrium degrees. For an atmospheric gas discharge plasma, frequent collisions between diverse particles are essential to sustain the plasma itself. The elastic collisions transfer energy and momentum between species. The inelastic collisions transfer not only energy and momentum but also charges through the processes of charge exchange, ionization, and recombination. Both of the elastic and inelastic collisions drive the

plasma system to be in an equilibrium state. From the aspect of energy transfer, each subsystem (electrons or heavy particles) obtains energy through the Joule heating process from the external power supply and loses the energy to the surroundings via radiation, conduction and convection processes. Simultaneously, there exist the energy exchange processes between the electron and heavy-particle subsystems through the local elastic and inelastic collision processes

One of the great problems in analysing gas discharges involves the vast number of species that can occur, even in very simple gas discharges, and the interactions between the various species. Indeed, gas discharges are very complex chemical systems. Therefore, let us try some initial categorization of the species we can expect to find.

2. PLASMA FUNDAMENTALS

When compared to fluid dynamics or electromagnetics in dielectric medium, plasma physics has a reputation for being extremely difficult to comprehend. There are two reasons for this. Because plasma is a charged fluid, its particles interact with one another not just through collisions, but also through long-range electric and magnetic fields. This is more difficult than simply addressing the symptoms. In an electron, for example, charged particles are released one at a time. Because plasma particles may migrate to protect one another, the fields are adjusted by the plasma itself. As a result of induced electric fields Second, the majority of plasmas are to be termed continuous fluids, they are too shaky and heated. For example, water ($\approx 3 \times 10^{22} \text{ cm}^{-3}$) or air ($\approx 3 \times 10^{19} \text{ cm}^{-3}$). Plasmas, with particle densities ranging from 10^9 - 10^{13} cm^{-3} , may not always behave like continuous fluids. The discrete character of the ions and electrons makes a difference; the kinetic theory of plasmas takes care of this type of detail. Fortunately, with a few exceptions, the fluid theory of plasmas is all that is needed to comprehend the behaviour of low-temperature industrial plasmas, and quantum mechanical effects of semiconducting substances are likewise absent.

2.1. QUASINEUTRALITY AND DEBYE LENGTH

Plasmas are charged fluids (interpenetrating fluids of ions and electrons) that follow Maxwell's equations in a convoluted fashion. The particle orbits are controlled by the

electric and magnetic fields in the plasma. The movements of the charged particles can generate charge bunches, which produce electric fields, or currents, which produce magnetic fields, all at the same time. As a result, the particle movements and electromagnetic fields must be solved in a consistent manner. Poisson's equation is one of Maxwell's equations:

$$\nabla \cdot D = \nabla \cdot \epsilon E = e(n_i - n_e). \quad (1)$$

Because the electric charges are explicitly indicated on the right-hand side, we usually choose ϵ_0 for ϵ , may be calculated from a potential V in electrostatic fields:

$$E = -\nabla V, \quad (2)$$

whereupon Eq. (1) becomes

$$\nabla^2 V = (e/\epsilon_0) (n_e - n_i). \quad (3)$$

This equation has a natural scale length for V to vary. To see this, let us replace ∇^2 with $1/L^2$, where L is the length over which V varies. The ratio of the potential energy $|eV|$ of an electron in the electric field to its thermal energy KT_e is then approximately

$$\left| \frac{eV}{KT_e} \right| = L^2 \frac{(n_e - n_i)e^2}{\epsilon_0 KT_e} \quad (4)$$

The Debye length, or natural length scale on the right, is defined by

$$\lambda_D = \left(\frac{\epsilon_0 K T_e}{n_e e^2} \right)^{\frac{1}{2}} \quad (5)$$

In terms of λ_D , Eq. (4) becomes

$$\left| \frac{eV}{KT_e} \right| = \frac{L^2}{\lambda_D^2} \left(1 - \frac{n_i}{n_e} \right) \quad (6)$$

Because if a significant potential is imposed within the plasma, such as with a wire linked to a battery, a cloud of charge will instantly form up around the wire to block out the potential disturbance, the left-hand side of this equation cannot be much bigger than 1. Eq. (5) has the value when the values of ϵ_0 and e are entered.

$$\lambda_D = 7.4 \sqrt{\frac{T_e(eV)}{n_e(10^{18}m^{-3})}} \mu m \quad (7)$$

Thus, λ_D is of order 50 μm for $KT_e = 4$ eV and $n_e = 10^{17} m^{-3}$ or $10^{11} cm^{-3}$, a value on the high side for industrial plasmas and on the low side for fusion plasmas. V would fluctuate across a distance in the plasma's main body, depending on the plasma's size. If we consider L to be on the order of 10 cm, which is a typical dimension for laboratory plasma, the factor $(L/D)^2$ is of the order of 10^8 , implying that n_i and n_e must be equal to within one part in 10^8 to keep the LHS minimal. The charge densities in the core of a plasma must be almost identical, therefore we may define a common density, termed the plasma density n , as either n_i or n_e . There exist, however, sheaths where L is the order of λ_D and the ratio n_i/n_e does not have to be close to unity.

This property of a plasma is known as quasineutrality. To keep the positive and negative species densities equal, charged particles will always find a way to travel. We've assumed the ions are single charged. If ions have a charge Z , then $n_i = Z n_e$. One seldom has a whole cubic on Earth, plasma density is commonly represented in cm^{-3} rather than MKS m^{-3} .

If L is the Debye length, then Eq. 6. The quasineutrality criterion may be broken. This occurs near a building's walls. probes put into the plasma a sheath of thickness next to the surface. A strong electric field is formed when ions outweigh electrons in $5\lambda_D$. Possibility is negative

compared to the plasma, therefore A Coulomb barrier repels electrons. Because electrons travel faster than ions, would leave the plasma favourably until repelled by this sheath drop. Eq. (3) shows Only $n_i > n_e$ gives $V(r)$ the proper curvature. is ion-rich sheath. As a result, relative to the walls or any electrically separated item (such a huge particle of dust or a wire). A drift probe Sheaths are significant in industrial plasmas and will be discussed later.

2.2. PLASMA FREQUENCY AND ACOUSTIC VELOCITY

In a continuous medium, waves are modest, repeating vibrations. We're used to hearing and seeing sound waves and electromagnetic (radio) waves in the air. We have sound waves and, well, water waves in water. Electromagnetic waves and two types of sound waves exist in a plasma, one for each charge species. The neutrals may, of course, have their own sound waves if the plasma is slightly ionized. Plasma waves or plasma oscillations are the sound waves that travel through the electron fluid. The characteristic frequency of these is often in the microwave region. Consider a group of electrons that have been displaced from their usual places. They'll leave a trail of positively charged ions in their wake, which will attract the electrons back. Without collisions, the electrons will go backwards, overshoot their original positions, and oscillate back and forth. Because the ions can't move on that time scale, they may be deemed immobile. The oscillation frequency, represented by ω_p , is calculated as follows:

$$\omega_p = \left(\frac{ne^2}{\epsilon_0 m} \right)^{\frac{1}{2}} \frac{rad}{sec} \quad (8)$$

In frequency units, this gives approximately

$$f_p = 9\sqrt{n(10^{12}cm^{-3})} \text{ GHz} \quad (9)$$

This is known as the plasma frequency, and it is solely determined by the plasma density.

In the ion fluid, the sound wave acts considerably differently. It has a characteristic velocity rather than a typical frequency, which is obviously considerably lower. The physical distinction is that when the ions migrate away from their equilibrium locations, more mobile electrons may accompany them and shield their charges. The shielding isn't complete, however, since electrons have random thermal movements that enable a little electric field to leak out of the

Debye cloud. The ion acoustic velocity, or ion sound speed c_s , is used to describe these ion acoustic waves.

$$c_s = \left(\frac{KT_e}{M} \right)^{\frac{1}{2}} \quad (10)$$

Where M is the ion mass. Note that C_s depends on T_e , not T_i , as in air, because the deviation from perfect Debye shielding depends on T_e . There is actually a small correction $\propto T_i$ which we have neglected because T_i is normally $\ll T_e$ in partially ionized plasmas. The hybrid ratio T_e/M permits ion sound waves to exist even when the ions are cold.

2.3. LARMOR RADIUS AND CYCLOTRON FREQUENCY

Many more sorts of wave movements are available when the plasma is embedded in a DC magnetic field (B-field) than those listed in the preceding section. This is because the B-field impacts charged particle movements and causes the plasma to become an anisotropic medium with a preferred direction along B. The ion or electron with charge q experiences a Lorentz force $qv \times B$, which is perpendicular to both the velocity and the field, as long as it is traveling. This force has no impact on the velocity component parallel to B, but it causes the particle to gyrate in a cyclotron orbit in the perpendicular plane. The cyclotron frequency, ω_c , is independent of velocity and solely relies on the charge-to-mass ratio:

$$\boxed{\omega_c = |qB|/m,} \quad \text{or} \quad \boxed{f_c = \omega_c/2\pi \approx 2.8 \text{ MHz/G}} \quad (11)$$

However, the radius of the gyro radius, also known as the Larmor radius or gyro radius r_L , is affected by velocity. A particle completes an orbit of length $2\pi r_L$ in time $2\pi/\omega_c$ if v is the velocity component in the plane perpendicular to B, thus $V_{\perp} = r_L \omega_c$ or

$$r_L = \frac{V_{\perp}}{\omega_c} \quad (12)$$

Since $\omega_c \propto 1/M$ while $v_{\perp} \propto 1/M^{1/2}$, r_L tends to be smaller for electrons than for ions by the square root of the mass ratio. Electrons are strongly constrained to move along B while gyrating rapidly in small circles in the perpendicular plane in processing plasmas with magnetic fields

of the order of several hundred gauss ($1 \text{ G} = 10^{-4} \text{ T}$), in which case heavy ions such as Cl (chloride) are not much affected by B , while heavy ions such as Cl are not much affected by B . In this instance, it is often easy to ignore the short gyro radius and focus just on the motion of the orbit's guiding centre. It's important to note that ions and electrons spin in opposing directions. Consider the moving charge as a current, taking into consideration the charge's sign, for a simple method to recall the direction. This current produces a magnetic field in the right-hand rule's direction, and the current must always be in a direction that produces a magnetic field that opposes the background magnetic field.

2.4. $\mathbf{E} \times \mathbf{B}$ DRIFT

The guiding centres of particles drift across B in response to applied electric fields E_{\perp} in magnetic fields so strong that both ions and electrons have Larmor radii significantly less than the plasma radius (the component perpendicular to B). The drift speed is determined by the following formula:

$$\mathbf{v}_E = \mathbf{E} \times \frac{\mathbf{B}}{B^2} \quad (13)$$

E_{\perp} has no effect on the velocity parallel to B . It's worth noting that v_E is perpendicular to both E and B , and that it holds true for both ions and electrons. If E is not constant over an ion's Larmor diameter, the ions experience an average E -field and drift slower than electrons. Heavy ions such as argon or chlorine may contact the wall before completing a Larmor orbit in fields of a few hundred gauss, as is typical in plasma processing. This is particularly true if they have been accelerated to an energy $\gg kT_i$ by E_{\perp} . In this example, the ions are essentially unmagnetized, but the electrons are highly magnetized and obey Eq. (13).

2.5. SHEATHS AND PRESHEATHS

Now we'll look at the specifics of how a sheath is created. Consider a wall with a plasma extending a long distance to the right ($x > 0$) at $x = 0$. We design an imaginary plane at $x = s$ that we might name the sheath edge. We would anticipate s to be on the order of λ_D (really, it is more like $5\lambda_D$) based on our explanation of Debye shielding. Outside the sheath ($x \geq s$), quasineutrality necessitates the use of $n_i \approx n_e$. Allow $V = 0$ to be the plasma potential there. We might have a charge imbalance within the sheath. To reject electrons, the potential in the sheath must be negative, which implies $V(x)$ must have a negative curvature. We can see that n_i must

be bigger than n_e from the one-dimensional version of Eq. (3). The density of electrons in a potential hill will be exponentially reduced if the electrons are Maxwellian:

$$\frac{n_e}{n_s} = \exp\left(\frac{eV}{kT_e}\right), \quad (14)$$

where n_s is the sheath edge density. Consider that ions traveling toward the wall are accelerated by the sheath's E-field and are not reflected, therefore the ion flux is constant when calculating the ion density. We may ignore T_i for now, but for reasons that will become evident later, we must suppose that the ions enter the sheath at a limited velocity v_s . The continuity equation is then

$$n_i v_i = n_s v_s \quad (15)$$

Conservation of energy gives

$$1/2 M v_i^2 + eV = \frac{1}{2 M v_s^2} \quad (16)$$

The last two equations give

$$\frac{n_i}{n_s} = \frac{1}{\left[1 - \frac{2eV}{M v_s^2}\right]^{1/2}} \quad (17)$$

Even for tiny values of $|V|$, just within the sheath, the sheath condition $n_i > n_e$ must hold. In such scenario, we may use Taylor series to extend Eqs. (14) and (17) to get

$$\frac{n_e}{n_s} = 1 + \frac{eV}{kT_e} + \dots, \quad \frac{n_i}{n_s} = 1 + \frac{eV}{M v_s^2} + \dots \quad (18)$$

Since V is negative, the condition $n_i > n_e$ then becomes

$$\frac{e|V|}{M v_s^2} < \frac{e|V|}{kT_e} \quad (19)$$

The sheath condition is then

$$v_s > (KT_e)^{\frac{1}{2}} = c_s \quad (20)$$

The Bohm sheath criteria specifies that ions must enter the sheath with a velocity at least equal to the acoustic velocity in order for a sheath of the desired shape to develop. Because it contains a net positive charge, such a Debye sheath is also known as an ion sheath.

The obvious issue now is: "How did the ions achieve such a massive, directed velocity, substantially more than their thermal energies?" In the quasineutral area of the main body of the plasma, there must be a tiny electric field that accelerates ions to an energy of at least $1/2KT_e$ toward the sheath edge. Only non-ideal events, such as collisions, ionization, or other sources of particles or momentum, may produce such an E-field. The presheath is a zone that stretches across distances on the order of the plasma dimensions. The pre-sheath field is faint enough that it may be created without violating quasineutrality. Even if nothing is done to improve the sheath drop, we can observe that ions automatically obtain a directed velocity by the time they contact the substrate in plasma processing. Though a voltage is placed between two walls or electrodes, an ion sheath will form on each wall, but the sheath drops will be asymmetrical, resulting in different electron fluxes to each wall, even if their area is the same. The ion fluxes to each wall, however, are the same ($= n_s v_s$), thus the total electron flow must match the total ion flux. Because the more positive electrode collects more electrons than the other, a current must flow through the biasing power supply.

If a presheath is required, the density n_s at the sheath edge must be different from the plasma density n in the plasma body. Because the ions' velocity at the sheath edge is c_s , their energy is $1/2Mc_s^2$, and there must be a potential drop of at least $1/2KT_e$ between the plasma's body and the sheath edge. Let's make $V = 0$ within the core plasma and $V = V_s$ near the sheath boundary. The electrons are still believed to be distributed in a Maxwellian manner:

$$n_e = n_0 e^{\frac{ev_s}{KT_e}}. \quad (21)$$

Because the integral of an exponential stays an exponential, it is a feature of a Maxwellian distribution that it remains a Maxwellian when put in a retarding potential at the same temperature, only the density changes. Because just a few electrons pass across the Coulomb barrier, the number of electrons traveling back from the sheath changes only little.

Thus, regardless of whether there are collisions or not, Eq. (21) holds throughout the plasma, presheath, and sheath. Eq. (21) informs us that $eV_s = -e|V_s| = -1/2KT_e$.

$$n_s = n_0 e^{-\frac{1}{2}} = 0.6n_0 \approx \frac{1}{2n_0} \quad (22)$$

Because there is no obvious dividing line between sheath and presheath, this is an estimate. We will utilize the simple relation $n_s \approx 1/2n_0$, where n_0 is the density in the primary plasma, in the future.

In conclusion, a plasma can survive with a material barrier only if a thin sheath develops around the boundary, separating the plasma from it. A Coulomb barrier, or potential drop, of many orders of magnitude exists in the sheath, repelling electrons and accelerating ions toward the wall. The sheath drop adjusts itself such that the ions and electron fluxes exiting the plasma are about equal, maintaining quasineutrality.

3. GAS DISCHARGE FUNDAMENTALS

3.1. Collision cross sections and mean free path

In a partly ionized plasma, we initially investigate collisions of ions and electrons with neutral atoms; collisions between charged particles are more intricate and will be discussed later. Ions and electrons do not detect the existence of a neutral until they are within an atomic radius of it, since neutral atoms have no external electric field. When an electron, for example, collides with a neutral, it will most of the time bounce off of it like a billiard ball. We can then assign an effective cross-sectional area, or momentum transfer cross section, to the atom, which means that an electron hitting such an area around the centre of an atom would have its (vector) momentum changed by a lot on average; a lot being a change comparable to the size of the original momentum. An electron's cross section is determined by its energy; therefore, a cross section is determined by the energy, or, on average, the temperature of the bombarding particles. Because atoms have a radius of roughly 10^{-8} cm (1 Angstrom), atomic cross sections

are typically about 10^{-16} cm^2 (1 \AA^2). Cross sections are often expressed in values of $\pi a_0^2 = 0.88 \times 10^{-16} \text{ cm}^2$, where a_0 is the radius of the hydrogen atom.

Cross sections tend to decrease with energy at high energies, ranging as $1/v$, where v is the entering particle's velocity. This is because the electron passes through the atom so quickly that the electric field of the atom's outermost electrons does not have enough time to modify the momentum of the passing particle. Depending on the intricacies of how the atomic fields are structured, (v) may be more constant or even go up with energy at low energies. The Ramsauer cross section, which occurs for noble gases like argon and takes a deep plunge about 1 eV, is a well-known example. Low-energy electrons may practically pass through a Ramsauer atom without even realizing it's there.

Ions have somewhat greater cross sections with neutrals because their masses are comparable, making it simpler for the ion to exchange momentum. Charge exchange collisions occur when ions collide with neutrals of the same species, such as Cl colliding with Cl^+ . An ion traveling near to an atom may ionize it by removing one of its outer electrons. The ion subsequently transforms into a fast neutral, whereas the neutral transforms into a slow ion. Although there is no significant momentum transfer, the change in identity gives the impression of a massive collision in which the ion has lost the majority of its energy. Charge-exchange cross sections (σ_{cx}) as big as $100\pi a_0^2$ are possible.

Unless dealing with a monoenergetic beam of electrons or ions, the collision probability $\langle \sigma V \rangle$, measured in cm^3/sec , where the average is calculated over a Maxwellian distribution at temperature KT_e or KT_i , is a far more relevant number. The collision frequency is thus $\langle \sigma V \rangle$ twice the density of neutrals; hence, the average rate at which each electron in that distribution collides with an atom is:

$$v_c = n_n \langle \sigma V \rangle \text{ per sec} \quad (1)$$

If the density of electrons is n_e , the number of collisions per cm^3/sec is just

$$n_e n_n \langle \sigma V \rangle \text{ cm}^{-3} \text{ sec}^{-1} \quad (2)$$

If the proper ion value of $\langle \sigma V \rangle$ is chosen, the same rate applies to ion-neutral collisions. A particle collides on average after traversing a distance of λ_m , which is known as the mean free path. Divide v by Eq. (1) (before averaging) to get distance, which equals velocity times time.

$$\lambda_m = \frac{1}{n_n \sigma} \quad (3)$$

This is the average mean free route for a Maxwellian distribution, not the mean free path for each particle velocity.

3.2. Ionization and excitation cross sections

If the incoming particle has enough energy, it may disrupt the electrons circling the atom, resulting in an inelastic collision. Occasionally, only the atom gets energized because the outermost electron is pushed into a higher energy level. The atom then decays into a metastable state or returns to the ground level, producing a photon of a certain energy or wavelength. Each such transition or spectral line that is typical of that atom has an excitation cross section. Higher-energy electrons may completely remove an electron from an atom, ionizing it. The ionization threshold for a hydrogen atom is 13.6 eV, as every freshman physics student knows; most other atoms have ionization thresholds somewhat greater than this figure. Eq. (3) relates the frequency of ionization to the ionization cross section σ_{ion} , which is clearly zero below the threshold energy E_{ion} . It rapidly grows over E_{ion} , then tapers down about 50 or 100 eV, then decays at very high energies because the electrons whiz past so quickly that their influence on the bound electrons is only felt for a fraction of a second. Because only a few electrons in the tail of a 4-eV distribution, for example, have enough energy to ionize, σ_{ion} rises exponentially with KT_e up to temperatures of around 100 eV.

Double ionizations in a single collision are relatively uncommon, however a singly ionized atom may be doubly ionized in a subsequent collision with an electron; for example, $Ar^+ \rightarrow Ar^{++}$. Almost all ions in industrial plasmas are only singly charged since they are kept cold. Some ions have an affinity for electrons and may hang on to an additional one, causing them to become negative. Examples are Cl^- and the compound SF_6^- . This phenomenon, which occurs at very low electron temperatures, has electron attachment cross sections.

3.3. Transition between neutral- and ion-dominated electron collisions

The collisionality of the electrons has a significant impact on the behaviour of a partly ionized plasma. We can calculate their collision rate with neutrals and ions based on the description above. Collisions between electrons are unimportant in this case; they simply shift the electrons' energy to keep them in a Maxwellian distribution.

The rate at which electrons and neutrals collide is given by

$$v_{en} = n_n \langle \sigma v \rangle_{en} \quad (4)$$

The total cross section σ for e-n collisions may be approximated by the elastic cross section, since inelastic processes have lower cross sections. The neutral density n_n is proportional to the gas's fill pressure n_{n0} . Pressure may be measured in Torr or mTorr, which is more convenient. The weight of a 1-mm high column of Hg is supported by a Torr of pressure, while atmospheric pressure is 760 Torr. A micron of pressure is sometimes known as a millitorr (mTorr). Some individuals prefer to measure pressure in Pascals, where 1 Pa equals 7.510 mTorr (about 7 times the size of a mTorr). The neutral density is p mTorr at 20°C and p mTorr pressure.

$$n_n \approx 3.3 \times 10^{13} p(\text{mTorr}) \text{ cm}^{-3} \quad (5)$$

The plasma density would be $n_e = n_i = n = n_{n0}$, if everything was ionized, but only for a monatomic gas like argon. $n = 2n_{n0}$ for a diatomic gas such as Cl₂. Is it true that e-i collisions are just as essential as e-n collisions? We may acquire a reasonable estimate of v_{en} by taking $\langle \sigma V \rangle$ to be $\langle \sigma \rangle \langle V \rangle$, which is $\approx 10^{-16} \text{ cm}^2$, and $\langle V \rangle$ to be the thermal velocity v_{th} , which is defined by

$$v_{th} \equiv \left(\frac{2KT}{m} \right)^{\frac{1}{2}},$$

$$v_{th,e} = \left(\frac{2KT_e}{m} \right)^{\frac{1}{2}} \approx 6 \times 10^7 T_{eV}^{\frac{1}{2}} \frac{\text{cm}}{\text{sec}} \quad (6)$$

then have

$$v_{en} \approx (3.3 \times 10^{13}) p \cdot (10^{-16}) \cdot 6 \times 10^7 T_{eV}^{\frac{1}{2}} \quad (7)$$

$$\approx 2 \times 10^5 P \text{mTorr} T_{eV}^{\frac{1}{2}}$$

(This formula is an estimate of order of magnitude and should not be utilized in precise calculations.) The frequency of electron-ion collisions is determined by

$$v_{ei} \approx 2.9 \times 10^{-5} \frac{n}{T_{eV}^{\frac{3}{2}}} \quad (8)$$

The ratio then gives

$$\frac{v_{ei}}{v_{en}} \approx 1.5 \times 10^{-10} \frac{n}{p} T_{eV}^{-2} \quad (9)$$

When this ratio is unity, the crossover point occurs with a density of

$$n_{crit} \approx 6.9 \times 10^9 PmTorr T_{eV}^2 \text{ cm}^{-3} \quad (10)$$

If $p = 3$ mTorr and $KT_e = 3$ eV, for example, the crossover density is $n_{crit} = 1.9 \times 10^{11} \text{ cm}^{-3}$. Thus, electron-ion collisions regulate High Density Plasma (HDP) sources operating in the high 10^{11} to mid- 10^{12} cm^{-3} range, while electron-neutral collisions control older low-density sources like the RIE running in the 10^{10} to mid- 10^{11} cm^{-3} range. The worst-case scenario occurs in the middle, when both sorts of accidents must be considered.

3.4. Mobility, diffusion, ambipolar diffusion

We can examine how collision rates impact plasma particle movements now that we know what they are. Electrons will flow in the E direction and carry a current if an electric field E (V/m) is applied to a plasma. We've shown how to calculate the specific resistivity η of a completely ionized plasma. The current density is then calculated as follows:

$$j = E / \eta \text{ A/m}^2 \quad (11)$$

In a weakly ionized gas, electrons lose energy in neutral collisions but receive it from the E-field between collisions, bringing their velocity to a steady state. Of course, the average drift velocity is proportional to E, and the proportionality constant is known as the mobility μ , which is linked to the collision frequency:

$$u = -\mu E, \quad \mu_e = \frac{e}{mv_{en}} \quad (12)$$

The magnitude of the elementary charge is always referred to as e. Ion mobility has a similar expression, but the ions will not carry much current. The electron flux Γ_e and the accompanying current density are calculated using

$$\Gamma_e = -n_e \mu_e E, \quad j = en_e \mu_e E, \quad (13)$$

and similarly for ions. When there is Debye shielding, how do these E-fields get into the plasma? If a voltage is applied to a section of the wall or an electrode within the plasma, electrons will migrate to shield it out, but a little electric field will always leak out due to the presheath effect. Only at high pressures can the presheath field be big. Inductive coupling, in which an external antenna or coil imposes a time-varying magnetic field on the plasma, and this field generates an electric field through Faraday's Law, may be used to apply greater E-fields. The plasma's electron currents will still attempt to shield out the generated field, but in a different manner; magnetic fields may limit this shielding. We'll go over this in more detail under Plasma Sources.

Plasma density is frequently nonuniform, with a high centre and a falling down toward the edges. Each species will disperse toward the wall, or more precisely, toward low-density areas. The diffusion velocity is proportional to the density gradient ∇_n , with the diffusion coefficient D serving as the proportionality constant:

$$u = -\frac{D\nabla_n}{n}, \quad D_e = \frac{KT_e}{mv_{en}}, \quad (14)$$

and similarly for the ions. The diffusion flux is then given by

$$\Gamma = -D\nabla_n \quad (15)$$

Note that D has dimensions of an area, and Γ is in units of number per square meter per second.

The total of the fluxes from mobility and diffusion toward the wall is then calculated.

$$\begin{aligned}\Gamma_i + \Gamma_e &\equiv 2\Gamma_a = n(\mu_i - \mu_e)E - (D_i + D_e)\nabla_n \\ \Gamma_i - \Gamma_e &\equiv 0 = n(\mu_i + \mu_e)E - (D_i - D_e)\nabla_n\end{aligned}\quad (16)$$

From these we can solve for the ambipolar flux Γ_a , obtaining

$$\Gamma_a = -\frac{\mu_i D_e + \mu_e D_i}{\mu_i + \mu_e} \nabla_n \equiv -D_a \nabla_n \quad (17)$$

We see that diffusion with the self-generated E-field, called ambipolar diffusion, follows the usual diffusion law, Eq. (15), but with an ambipolar diffusion coefficient D_a defined in Eq. (17). Since, from (12) and (14), μ and D are related by

$$\mu = eD/KT, \quad (18)$$

and μ_e is usually much greater than μ_i , D_a is well approximated by

$$D_a \approx \left(\frac{T_e}{T_i} + 1\right) D_i \approx \frac{T_e}{T_i} D_i \quad (19)$$

implying that plasma loss to the walls is slowed to the slower species' loss rate, which is adjusted by the temperature ratio.

4. ATOMIC COLLISIONS AND SPECTRA

4.1. ATOMIC ENERGY LEVELS

When electrons or nuclei in an atomic or molecular system shift between different energy levels, electromagnetic radiation or photons are produced. To completely characterize the interaction between materials and electromagnetic radiation, a thorough theory of radiation is required, which will not be covered in this session. However, a minimal number of principles will be described in order to learn the fundamentals of radiation physics.

We'll start with the interaction of electrons in atoms' bound states with electromagnetic radiation. When bonded electrons in an atomic system shift between different energy levels, they generate electromagnetic radiation, or photons. The electromagnetic interaction between different bound electrons and nuclei determines the energy levels of each atomic system.

Except for the simplest atomic system, the hydrogen atom, calculating atomic energy levels requires solving a Schrodinger equation for a multiple particle system (nucleus and electrons), for which there is no perfect solution. To compute the atomic energy levels, numerous approximation techniques have been devised; nowadays, the energy levels of many atomic systems are recognized and reported in the form of a Grotrian diagram. LS (also known as Russell-Saunders) coupling is one method to indicate the different energy levels in the Grotrian diagram. However, it should be noted that the LS coupling scheme does not always identify each energy level in a unique way, therefore it should be used with caution. Each state is designated by its orbital angular momentum and spin state, as well as each electron's configuration state, according to the LS coupling scheme.

4.2. ATOMIC COLLISIONS

In a homogenous plasma, energetic electrons collide with neutrals, resulting in excited neutrals, atoms, free radicals, ions, and more electrons. The plasma chemistry is complicated and fascinating because of these electron collision reactions. The electron-particle collision may be considered as an elastic collision event due to the high mass difference. There are a number of different electron-atom collision reactions listed:

1. Excitation processes
 - a. Electron impact ionization
 - b. Electron impact excitation
 - c. Electron impact dissociation of diatomic molecules
 - d. Electron metastable ionization
 - e. Metastable-neutral ionization
2. Relaxation and Recombination Processes
 - a. De-excitation
 - b. Electron-ion recombination
 - c. Radiative recombination

- d. Electron attachment
- e. Ion-ion recombination

5. MOLECULAR COLLISIONS AND SPECTRA

When molecules shift between different energy levels, they produce photons, much like atoms. Additional kinds of motion are available in molecules, though. They are molecular rotation and vibration. Because vibrational and rotational states are inefficient, only a small amount of energy is linked. This weak coupling may be thought of as a momentum restriction, meaning that the low mass, high velocity electron cannot trigger certain states where momentum must be transmitted to an atom. A single quantum is transmitted in a typical electron excitation of rotating states. Because the quantum for rotating states is on the order of one milli-eV, only a little amount of energy is transmitted. Only a single quantum is normally transmitted in electron impact excitation of vibrational states. The energy of the vibrational quanta is on the order of 0.1 eV. The vibrational excitation of molecules, in which the electron binds to produce a short-lived negative ion, is an exception. Because the negative ion has a different interatomic spacing than the neutral state, when the electron departs, the molecule has a different bond length than the neutral state. The link functions as a spring, transforming the energy into a large number of vibrational quanta. The excitation of rotational and vibrational states is often not substantial in the discharges used in microelectronics processing since a typical chemical bond is on the order of 4-5 eV. However, owing to these extra modes of motion, the energy levels of molecules are more complex.

5.1. MOLECULAR ENERGY LEVELS

a. Electronic energy level

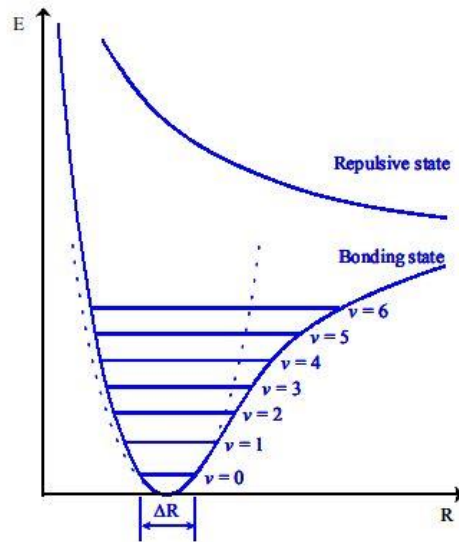


Figure 1: Electronic states of a molecule from [3]

b. Vibrational energy level

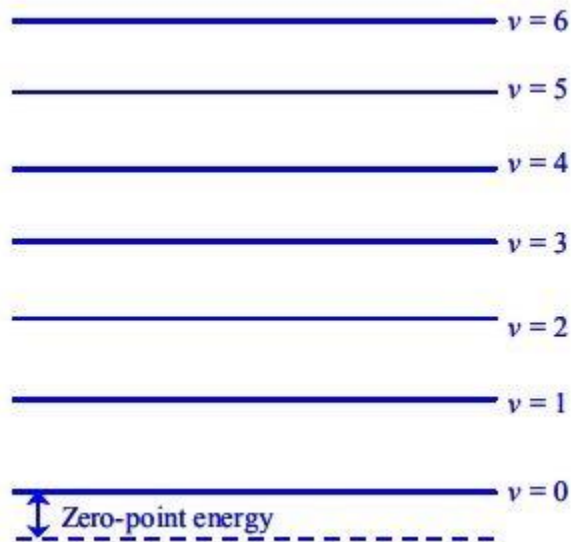


Figure 2: Vibrational energy levels from [3]

c. Rotational energy level

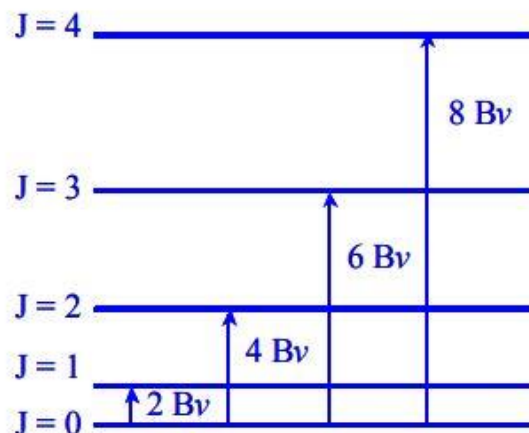


Figure 3: Rotational energy levels from [3]

5.2. SELECTION RULE FOR OPTICAL EMISSION OF MOLECULES

For practical applications, the following (approximate) selection rules are given for molecular transitions:

Change in orbital angular momentum: $\Delta\Lambda = \pm 1$

Change in spin angular momentum: $\Delta S = 0$

The selection rule for 'v to v'' is: $\Delta v = \pm 1$

The selection rule for 'J to J'' is: $\Delta J = \pm 1$

In addition, for transitions between Σ states, the only allowed transitions are $\Sigma^+ \rightarrow \Sigma^+$ and $\Sigma^- \rightarrow \Sigma^-$; and for homonuclear molecules, the only allowed transitions are $g \rightarrow u$ and $u \rightarrow g$.

5.3. ELECTRON COLLISIONS WITH MOLECULES

The interaction time of an e- with a molecule is:

$$t_c \sim 10^{-16} - 10^{-15} \text{ s}$$

The typical time for a molecule to vibrate is:

$$t_{\text{vib}} \sim 10^{-14} - 10^{-13} \text{ s}$$

The typical time for a molecule to dissociate is:

$$t_{\text{diss}} \sim t_{\text{vib}} \sim 10^{-14} - 10^{-13} \text{ s}$$

The typical transition time for electric dipole radiation is:

$$\tau_{\text{rad}} \sim 10^{-9} - 10^{-8} \text{ s}$$

The typical time between collision in a low-pressure plasma is τ_c

These time scales are:

$$t_c \ll t_{vib} \sim t_{diss} \ll \tau_{rad} \ll \tau_c$$

a. Frank-Condon principle

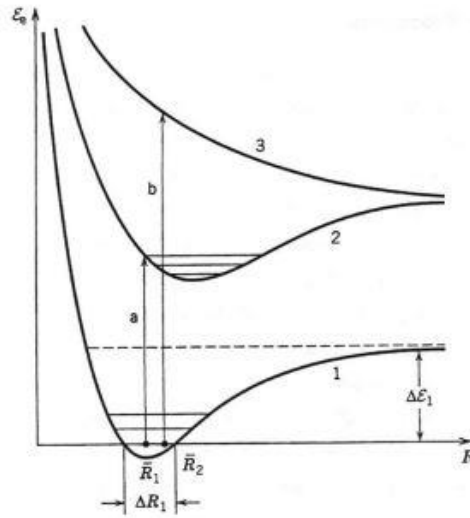


Figure 4: Frank-Condon or adiabatic transition from [3]

b. Dissociation

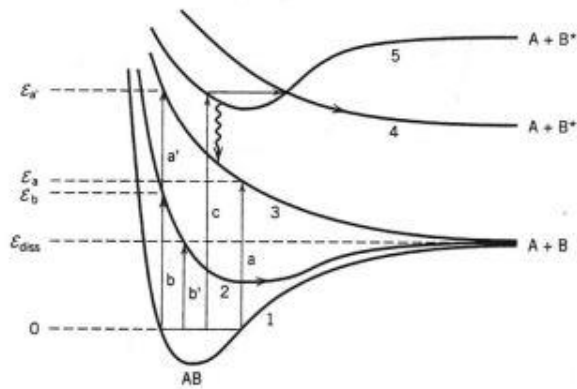


Figure 5: Dissociation process from [3]

c. Dissociative ionization and dissociative recombination processes

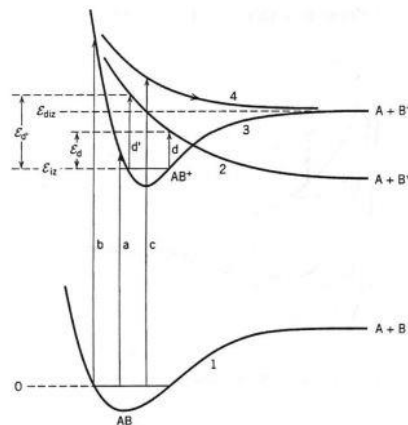


Figure.6: Dissociative ionization and dissociative recombination process from [3]

d. Dissociative electron attachment

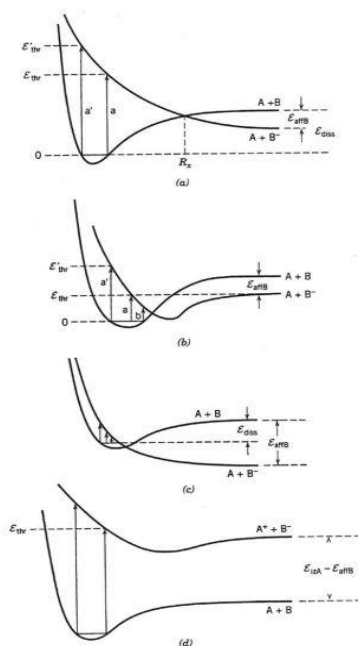
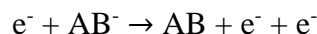


Figure 7: Electronic attachment process (a) A repulsive state (b) an attractive state (c) Repulsive state with slow electrons (d) Polar dissociation from [3]

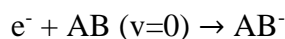
e. Electron impact detachment

When an electron collides with a negative ion, the electron might detach, resulting in a neutral and one extra electron. The electron affinity of the negative ion is crucial in this case.



f. Vibrational and rotational excitation

Molecules may be excited into higher vibrational and rotational energy levels by electrons with enough energy. This is usually a two-step process, with the electron being trapped first (forming a negative ion) and subsequently detached to produce a vibrationally excited molecule.

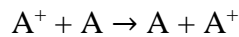


5.4. HEAVY PARTICLE COLLISIONS

Ion-ion, ion-neutral, and neutral-neutral collisions are all heavy particle collisions. These substances all have far lower temperatures than electrons, thus they travel much slower. The following are some of the most significant heavy particle collisions:

a. Resonant and non-resonant charge transfer

The importance of resonant charge transfer in the production of fast neutrals and slow ions, which would alter the overall environment plasma's chemical reactivity nearer the surface.



Non-resonant charge transfer may occur between atoms/molecules that are unlike each other or between an atom and a molecule.

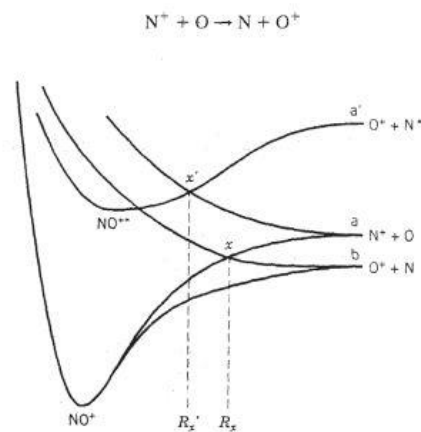
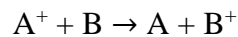
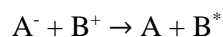


Figure 8: Nonresonant charge transfer processes from [3]

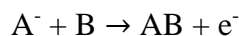
b. Positive and negative ion recombination

Ion-ion recombination is a sort of charge transfer that may be the major process for the loss of negative ions in a low-pressure electronegative plasma, as detailed in Atomic Collisions and Spectra.



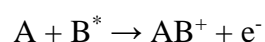
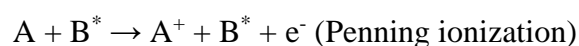
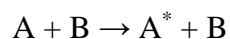
c. Associative detachment

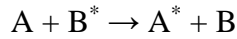
Figure depicts the associative detachment process. The dissociation process changes depending on the energy level of AB^- .



d. Transfer of excitation

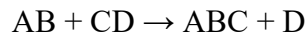
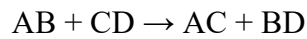
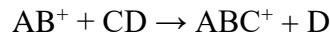
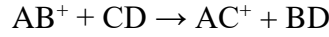
Transfer of excitation, including Penning ionization, may occur in the plasma, as explained in Atomic Collisions and Spectra.





e. Rearrangement of chemical bonds

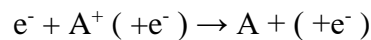
Chemical bond rearrangement may also occur in plasma, resulting in a more complicated composition.



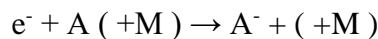
f. Three-body processes

Three body collisions, as detailed in Atomic Collisions and Spectra, are crucial processes that preserve energy and momentum while allowing complicated chemical reactions to occur in the plasma gas phase.

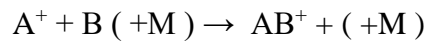
- Electron-ion recombination



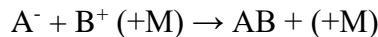
- Electron attachment



- Association



- Positive-negative ion recombination



5.5. GAS PHASE KINETICS

Inelastic collisions between energetic electrons and thermal energy neutrals are nearly completely responsible for the peculiar chemical processes that occur in a plasma. The inelastic scattering generates a slew of excited states, which subsequently relax and/or interact as a result of collisions between particles or with the reactor's walls.

6. IONIZATION IN GASES

A body of gas must contain free electric charges if large electric and magnetic body forces are to be applied on it. These may be obtained by thermally, chemically, electrically, or irradiating the gas, or by combining distinct methods. Regardless of the method of production, sources of positive ions and electrons. The presence of free charges in a compressible fluid makes it far more difficult to compress. Thermodynamics, particle kinetics, and continuum dynamics are all aspects of thermodynamics. Several exceptional texts consider Various facets of these

themes are discussed in depth, and we will do so here. Only bring up a few key ideas for debate. The atomic scale is the subject of this chapter. Ionization processes and the ionization equilibrium levels they may achieve. The fundamentals of ionized gas continuum dynamics. Most of the acceleration ideas produced in following chapters will be applicable to most of the acceleration concepts introduced in this chapter and will be. There are a variety of topics explored there in diverse circumstances.

6.1. ATOMIC STRUCTURE

Without delving too deeply into atomic physics¹, we must agree on a useful conceptual model of the atoms, molecules, and ions that make up the ionized gases of interest. For our purposes, an atom is made up of a small compact nucleus of Z protons and Y neutrons ($Z \approx Y$; total dimension $\approx 10^{-12}$ cm) surrounded by a much larger region ($\approx 10^{-5}$ cm) in which Z electrons arrange themselves in specific but diffuse configurations depending on the atom's internal energy and internal angular momentum. Bohr and Sommerfeld described these electronic configurations in terms of satellite-like orbits.

The deeper characteristics of atomic structure demand a more complex wave-mechanical, or probabilistic, description. For now, all we need to know is that the atomic electron distribution has a minimum energy configuration, known as the ground state, and that an atom may absorb energy to adopt other configurations only in discrete quantities (quanta) and with discrete changes in internal angular momentum. Normally, such energy increases are represented by just one of the bound electrons at a time being adjusted.

With each subsequent energy increment absorbed, that electron is pushed farther away from the nucleus, until it ultimately detaches itself from the atomic system, leaving behind a configuration of net positive charge, i.e., a positive ion. A so-called grotrian diagram is used to depict the evolution of these electronic energy levels to the ionization limit. The ionization potential S is the total energy increase required to remove one electron, and it varies greatly from one gas to the next. In general, noble gases have high ionization potentials, whereas alkali vapours have low ionization potentials.

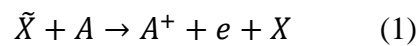
This ionization energy may be absorbed in a single atomic event, or the electron can be increased to the ionization limit by a series of operations. Because of the propensity for spontaneous radiative decay from one of the intermediate levels to disrupt the sequence of

absorptions, the latter route is less possible. The usual lifespan of an excited state against spontaneous decay is set at a second. There are certain situations when stepwise ionization is critical, but for now, we'll assume a single-increment procedure.

6.2. IONIZATION PROCESSES

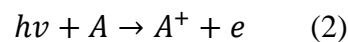
The energy increment required for ionization of a component atom in a gaseous environment may be given in a number of ways.

- a. It's possible that the atom will collide with another particle with a sufficiently high relative kinetic energy. The "reaction" notation may be used to represent this.



where \tilde{X} is a high-relative-kinetic-energy particle that might be another atom, an ion, or an electron.

- b. An electromagnetic photon with a sufficiently high frequency may be absorbed by the atom:

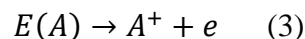


where h = Planck's constant (6.62×10^{-34} joule-sec)

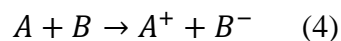
ν = frequency of radiation absorbed

$h\nu$ = corresponding energy increment delivered

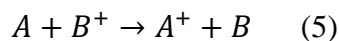
- c. A high electric field may take an electron from an atom forcefully.



- d. An electron may be lost in some sensitive atoms due to a strong valence contact with another atom:



Or with an ion:



There are many techniques to trigger the ionization process in each of these groups. The inelastic collision process might, for example, be gas-kinetic, i.e., a simply thermal collision, or it could be with a viscous collision.

With a cosmic charge, a charged particle is propelled in an external electric field. particle, or a result of radioactive decay. The source of radiation for the equation might be external (photoionization) or internal (resonance) to the gas. trapping. The electric field for third equation might be provided externally as a radio-frequency propagating field, a slowly changing field, or a stable field

A localized net charge or an electromagnetic wave train1 might cause this. density inside a gaseous substance (3) and (4) are charge-exchange reactions.

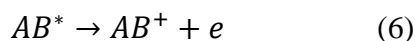
Depending on the particles, 5th equation may continue in a variety of ways involved.

Ionization of gas molecules may happen in a variety of ways.

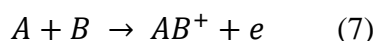
internal rotation and a variety of processes, with the extra possibilities that internal rotation and a variety of processes provide.

The molecular structure's vibration modes may be accessed over the internet.

For instance, consider the electrical structure.

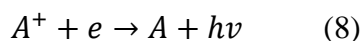


where AB* signifies a hyperenergetic molecular state that gives up its excitation to ionization spontaneously. A molecular ion-electron pair is the typical result in a few rare exothermic chemical reactions

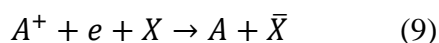


The existence of material surfaces close to the gas body may further confound the image. Some of the aforementioned gas-phase processes may be catalytically enhanced by such solid surfaces, or they may be prolific providers of free electrons or positive ions through bombardment, emission, photoelectric emission), charge-transfer trapping, or thermionic emission.

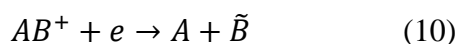
A. Radiative recombination:



B. Three-body recombination:



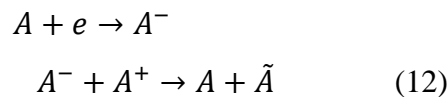
C. Dissociative recombination:



D. Dielectronic recombination:



E. Electron attachment followed by negative-ion recombination:



This list is, once again, oversimplified. The product atom in (8) may be left in any of a number of excited states, from which it can decay by radiation or future collision. The third body in (9) might be another atom, such as A, an impurity particle, a wall, or something else entirely. Many atoms may produce stable molecular ions in reaction (10) and it is not limited to molecules. The goods may be left in a number of exciting states here and in (11). In (12), there are alternative second stages that include excited states and/or radiation. The relative relevance of the different processes, like with ionization reactions, depends on the specific gas involved, its temperature, density, and surrounding conditions of boundaries, applied fields, and so on.

6.3. EQUILIBRIUM IONIZATION OF A GAS

Each of the above-mentioned ionization and recombination processes might work in the opposite way. Every such process—indeed, every atomic excitation process, whether involving ionization or not—must be exactly balanced by its reverse process in a body of gas in complete thermodynamic equilibrium. This condition of detailed physical balancing provides the basis for applying statistical mechanics to the calculation of the equilibrium composition of the gas. The aforementioned number density ratio in equilibrium is simply supplied by the corresponding ratio of the sums of accessible energy levels, correctly weighted by degeneracies and by the Boltzmann factors in the relative energies of those states, according to statistical mechanics principles.

6.4. IONIZATION OF A GAS MIXTURE

In many practical circumstances, ionization of a mixture of gases with significantly varied ionization potentials is required. Many practical issues, for example, use air as the working fluid, which produces a plethora of atomic, molecular, and ionic species at high temperatures. Over twenty reaction equations must be solved concurrently to provide a credible approximation of the equilibrium ionization of air.

Ionization of a gas with a relatively high ionization potential that contains an unavoidable trace of an easily ionized impurity, or to which such an easily ionized substance has been purposefully added to increase its ionization level and thus its electrical conductivity, is a somewhat less tedious problem of practical interest.

In order to maintain enough gas conductivity at bearable temperature levels, various magnetogasdynamics gear, particularly electric generators and steady flow accelerators, use

this seeding process.

The widespread occurrence of the exceptional scenario when the temperature is so low that both species are only weakly ionized demonstrates the essence of reaction coupling. Let us pretend for a minute that each of the species A and B occupies similar but separate containers of the same volume¹ with the same particle density as the combination and at the same low temperature to get reference values.

The physical rationale is that the free electrons given by either specie are accessible for recombination with ions of the other species as well as their own, and this scenario selectively discriminates against the net ionization level of the specie with greater ionization potential.

7. collision in an ionized gas:

Almost every attribute of interest to engineers in a gas is derived from a myriad of atomic-scale interactions, or collisions, that occur constantly inside the gas. Mass diffusion, viscous friction, thermal conduction, electric current conduction, and other transport processes are accomplished by the migration of atomic particles within the gas, or by the transfer of their momenta and energy through the gas and are thus primarily controlled by the frequency and effectiveness of their collisions. The effectiveness of the collisional communication system among the atomic particles determines the pace at which the gas can adapt to changes in its surroundings and reach a new equilibrium state after being disturbed from one. As previously stated, the equilibrium state is a balance between collision events that generate a certain set of species products and other collisional events that reverse the reactions. Even continuum thermodynamic properties like pressure, temperature, and entropy are macroscopic manifestations of atomic collision processes, and kinetic theories of neutral gases have been used to establish a correlation between collisional mechanics and these thermodynamic properties with considerable elegance.

7.1. Atomic collision Nomenclature

As important as atomic collision data is for a complete understanding of ionized gas behaviour, collecting and cataloguing it is incredibly challenging. Even in the most basic ionized gas, which consists of electrons, single positive ions, and neutral atoms, there are six possible particle collisions to consider: electron-ion, electron-atom, electron-electron, and so on. With the exception of electron-electron collisions, the interaction may produce a wide range of outcomes. The event may be identified in the first place by one of three forms of energy

exchange.

- a. Elastic, in which the two particles' entire kinetic energy is conserved, and their original charges are maintained.
- b. Inelastic, in which kinetic energy is transferred into some internal mode of one or both colliding particles.
- c. Super elastic, in which one or both colliding particles deliver some of their internal energy to the kinetic energy of the system, as in collisional deexcitation, or surrender some potential energy, as in the electron-ion recombination event.
- d. Radiative, where a charged particle is propelled through the potential field of another particle and emits energy in the electro-magnetic spectrum.
- e. Charge-reactive, when electric charge is transferred from one particle to the other in an otherwise elastic event.

Not just binary collisions, but also three-body collisions including a "catalytic" particle that assists in momentum conservation, may be included in the above list.

The specific consequences of each of these collision classes are highly influenced by the colliding particles' relative kinetic energy¹, their impact parameter, and their internal states of excitation. Diverse atomic species colliding under otherwise equal conditions produce strikingly different effects. For example, with the same energy, elastic electron collisions on argon atoms are considerably different from those on helium; electronic excitation collisions are principally determined by the specie excited's unique atomic level structure; and so on. Much of the atomic collision picture's intricacy may be attributable to the interactions' basically quantum-mechanical origin. In many cases, the wavelike behaviour of the interacting particles totally obscures fundamental Newtonian notions and rigid-body mechanics.

Unfortunately, there is a scarcity of experimental data. At energies above 10 eV¹, atomic collision phenomena have been extensively studied using atomic¹ ionic, and electronic beams scattered in target chambers. However, at lower energies corresponding to ionized gas temperatures of engineering interest, these techniques become more difficult, and the results less certain. Extrapolation of high-energy particle beam data to extremely low energies may be deceptive, yet again, due to quantum-mechanical phenomena at work. Direct measurement of desirable ionized gas transport coefficients and reaction rates in ionized gases is only possible in a few basic scenarios and extrapolating such findings to less idealized settings is dangerous. In the subject of atomic collisions, vigorous theoretical and experimental study continues, but our current knowledge of these crucial processes is insufficient, which will hamper our future macroscopic computations. We will simply try to present a little terminology and physical

principles, as well as show a few common findings here.

7.2. Electron-Atom collisions

Because electrons are the most mobile particles in an ionized plasma, their mobility has a significant impact on transport characteristics and reaction rates. Because the majority of electron collisions in a gas occur with neutral atoms if it is just slightly ionized¹, the electron-atom cross sections are important in identifying these gas parameters.

ELASTIC

Elastic electron-atom cross sections have a strong energy dependency and an equally severe angular scattering profile in the low energy, or thermal, region, and vary by many orders of magnitude from one atom.

We include both inelastic collisions that leave the atom in an excited bound state in this category, where e signifies an incoming electron with kinetic energy at least equal to the excitation or ionization potential involved. These forms of inelastic electron-atom collisions may be a key influence in setting the free-electron energy distribution in an ionized atmosphere, in addition to their main function of supplying excited atoms and new ion-electron couples. Because most excitation and ionization potentials are a few electron volts or less, each inelastic event depletes the electron component's mean thermal energy per particle. In reality, for gases with low electron temperatures, such as $T_e < 10^4 \text{K}$: only the most energetic electrons in the distribution can complete these events at all and, as a result, the distribution rapidly reverts to the low energy end. As a result, the combined impact of several such collisions suppresses the electron temperature and somewhat distorts the distribution toward the low energy end.

Transitions between resonances When compared to elastic collisions, the angular dependence of the scattered electron trajectory tends to concentrate more in the forward direction, and this tendency increases with incident energy.

SUPERELASTIC

Collisions in which an electron gains kinetic energy at the cost of an excited atom's internal energy are known to occur. Experiments on specific cross sections are scarce¹, but mercury vapor has shown values as high as 10^{-15} cm^2 for certain atomic electronic transitions. Barring unusually large values of Q_1 , this type of collision will have little effect on the electron energy distribution in mildly ionized gases with a small fraction of atoms in excited states.

RADIATIVE

In theory, the electron may interact with the atomic potential field electromagnetically, but since the neutral atom field is very weak and has a very limited range¹, the effective cross section is small, perhaps 10^{-22} cm² or less.

CHARGE-REACTIVE

The incoming electron may be trapped by the atom until specific conditions are met, resulting in a negative ion. This is known as electron attachment¹, and it may need the involvement of a third body_ to dispose of the net potential energy relinquished. Although it has been found in atomic oxygen, it is more prevalent in specific polar molecules such as O₂, NH₃, H₂S, SO₂, and N₂O¹. Although experimental data is limited, O₂ shows a cross section of 10^{-19} s cm² with an uneven energy dependency.

7.3. ION-ION AND ELECTRON-ELECTRON COLLISIONS

Electrons in an ionized gas are energetically shielded to some degree from heavier particles due to their mass disparity¹ and depend significantly on interspecies collisions to set their energy distribution in a particular environment. Ions communicate better with other heavy particles, but because of the extended range of ion-ion coulomb interactions, their interspecies collisions have a significant impact on their energy distribution.

ELASTIC

Despite the fact that ion-ion and electron-electron collisions have the same coulomb potential fields as electron-ion interactions¹, they differ in a few keyways. The energy transfer is vastly more efficient¹ because of the equal masses, which is $Q(p) \propto 1/p$; $Q(J) \propto 1/J$; In a centre-of-mass frame of reference, θ and the scattering angles of the two particles are equal. Second, if the two particles are exactly the same, both classical indistinguishability [$q(\theta) = 9(1 - \cos\theta)$] and quantum-mechanical exchange effects (mott scattering) appear. With these exceptions¹, the cross-section's energy and angular dependence mirror the electron-ion scattering described above.

Only at energies above several electron volts can two heavy charged particles of the same sign approach close enough together to disturb either electronic structure¹, and even then, the

interaction is inefficient.

SUPERELASTIC

The same comments apply to inelastic.

RADIATIVE

There is no net charge acceleration or dipole moment change when two similar charges are simultaneously deflected. As a result, there is no first-order bremsstrahlung. Quadrupole radiation and relativistic effects may occur; however, they are insignificant in our study regimes.

7.4. ATOM-ATOM COLLISIONS

ELASTIC

In the context of the kinetic theory of gases, the elastic collisions of neutral atoms have been extensively studied. For a variety of interatomic potential functions, ranging from simple rigid spheres to the vander waals and Lennard-Jones models, detailed calculations of mean free paths, transport processes¹, rate processes, and so on are available. This potential typically combines a weak attraction of two dipoles (r^{-6}) with a hard-core repulsion of much shorter range (r^{-12}).

Quantum-mechanical effects are suppressed because the momenta of most heavy particles in a high-temperature gas are large enough that their associated de Broglie wavelengths, $\lambda = h/mv$, are small in comparison to atomic dimensions. In the vast majority of cases, a traditional approach is perfectly adequate.

Although individual cross section determinations at low energies are difficult, macroscopic measurements of transport coefficients agree well with classical theories. For common gases, the effective cross sections calculated from these experiments range from 1 to $11000 \times 10^{-16} \text{ cm}^2$, depending on the species' electronic and molecular structure. Except at very low energies (0.1 eV), where the attractive portion of the interatomic potential may slightly increase the cross section¹, typically a: c-H, energy dependence is usually quite mild¹. For individual binary collisions of common gas atoms over the energy range below 1 eV, molecular beam techniques

have advanced to the point where specific cross section vs. energy and angular scattering profiles can be traced. Although interesting quantum-mechanical resonances are being identified, it is unlikely that any major revisions in the magnitudes of distribution-average cross sections for gas transport calculations will be required, as the primary goal of these experiments is to gain a better understanding of the details of atomic structure and interactions.

INELASTIC

The available atomic beam data on atom-atom collision excitation or ionization is almost entirely at very high energies. Extrapolation back through the low energy range to threshold yields reasonable values, but only swarm averages provide direct confirmation. According to one viewpoint, colliding atoms are simply carriers that transport bound electrons into the specific interaction, implying that, above a certain threshold, an atom-atom collision is roughly as effective as an electron-atom collision at the same relative velocity. As a result, we estimate excitation cross sections of 10^{-20} cm² and ionization cross sections of 10^{-11} cm² in the low energy range. Just beyond threshold, the energy dependence is most likely linear, although the amplitude of the slope may be species dependent. The noble gases argon, krypton, and xenon have slopes of 10^{-19} cm²/ev, according to recent shock tube measurements.

RADIATIVE

No occurrences of this kind are predicted or seen due to the narrow range of atomic fields.

CHARGE-REACTIVE

Because the creation of a negative ion is required for this interaction, it can only take place in particular electronegative gas mixtures, which are outside the scope of this outline.

7.5. COLLISIONS OF ATOMS

The interaction field between an ion and an atom is the same as that between a charge and an induced dipole, which is $1/r^2$ and hence somewhat larger than that between two atoms but still fairly short range. The properties of elastic, inelastic, and super elastic collisions should

therefore be similar to those of atom-atom collisions. A monoenergetic ion beam is easier to prepare experimentally than an atomic beam, and the cross-sectional data may be more trustworthy. Unfortunately, the energy range below 5 eV is still difficult to define, and there is little data available.

ELASTIC

With total cross sections in the range 10^{-15} to 10^{14} cm², ion beam studies down to 5 eV demonstrate angular distributions with substantial forward scattering preference.

- As energy declines in this range, the angular dependence becomes more isotropic, and the size of the total cross section rises significantly.

INELASTIC

The cross sections increase rapidly from zero at the threshold energy with a slope typical to the specie and transition, then flatten and maybe decline in the upper energy ranges beyond our interest, much as they do in the atom-atom situations.

SUPER ELASTIC

Because the bound levels of an atom and its initial ion differ significantly from those of atoms, the latter must be considered important processes. Little is known about the size of these cross sections, apart from the thorough balancing considerations for a gas in equilibrium.

RADIATIVE

Bremsstrahlung from this source is insignificant due to the short-range interaction and massive mass of the ion.

CHARGE-REACTIVE

The charge -exchange event is perhaps the most essential of all ion-atom collisions.

In many electromagnetic plasma accelerators, this mechanism or its inverse offers an effective coupling between the ionized- and neutral-gas components. This event's cross section normally reaches a maximum in the thermal energy range, where it may significantly surpass the elastic cross section, say 10^{-15} to 10^1 cm², and then progressively falls with energy. Forward scattering prevails, allowing for the generation of high-energy atomic beams. Because the product particles of a charge-exchange interaction and an elastic ion-atom collision are the

same, these two cross sections are typically added together to form a single effective scattering cross section.

OTHER INTERACTIONS

The preceding list is meant to give you an idea of the wide range and complexity of collisional events that may occur inside an ionized gas body, contributing to thermodynamic, transport, and kinetic processes. It is far from complete. All incident photon interactions, such as photoionization, photoexcitation, inverse bremsstrahlung, and others, which complement radiative collisions; molecular interactions, which bring into play a variety of rotational and vibrational degrees of freedom that may participate in inelastic events; and the majority of interactions involving negative ions, are notable omissions. Details on this and other less frequent collisions may be found here. The reader is directed to the References and the bibliographies within for explanations of experimental and theoretical methodologies, as well as tabulations of cross-sectional data.

8. Gaseous electronics and gas lasers

8.1. GAS DISCHARGE SPECIES

Neutrals

Starting with a unionized gas, we may have simple atoms, such as those found in rare gases and metal vapours, or relatively simple molecules, such as XY or XZ. Typical pressures are in the few torr range (1 torr equals 1 mm Hg), but they may vary from a few microns (10^{-3} torr) to atmospheric pressure (760 torr) and even tens or hundreds of atmospheres. Neutral densities may then fluctuate throughout a range of roughly 10^8 , but at a few torr pressure, neutral densities will be in the 10^{22} - 10^{23} range. At 1 torr and 0°C , the gas has a volume of 3.54×10^{22} m³.

Charged Particles

We'll have electrons and a variety of ions since the medium is ionized. The electron densities we predict for normal gas discharges will be in the range of 10^{16} to 10^{20} m⁻³. We will have positive ions, but we may also have negative ions owing to chemical reactions. Furthermore, the ionic species, both positive and negative, might vary significantly from the neutral species, particularly when the gases are molecular. Discharges in He, for example, will result in the presence of He⁺ ions. Furthermore, discharges of N and O (air) produce a large number of particles.

N, N₂, O, O₂, NO, O₂, N₂O, O₃, and more species are among them. Each ion species has an effect on the electrical characteristics of the discharge, although electrons normally take the lead in this respect. Furthermore, we are frequently interested in "quasineutral" plasmas, which are plasmas that do not have substantial electrostatic forces. This means that the net charge density is close to zero, or that the total of the densities of electrons (n_e) plus negative ions (n_-) is close to the sum of the densities of (singly ionized) positive ions (n_+).

$$n_e + n_- - n_+ \ll n_e$$

Excited Species and Photons

The existence of excited neutral species (X^* and YZ^*), as well as potentially excited ionized species (X^+), is clearly of paramount relevance for lasers, light sources, and other devices where quantum effects occur. The photons that are emitted as a consequence are crucial, as is the likelihood of photon absorption leading in photo excitation, photo ionization, or stimulated emission.

The huge number of species that may arise, even in relatively basic gas discharges, and the interactions between the numerous species, is one of the major challenges in assessing gas discharges. Gas discharges are, in fact, very complicated chemical processes. As a result, let us attempt some preliminary classification of the species we may anticipate encountering.

8.2. Interactions Between Species

The interaction between these species is the true foundation of our research of gas discharges. So, let's take a look at some of the most essential exchanges that occur. Super elastic collision between an excited atom with an electron result in a de-excited atom and a fast electron in electron collisional excitation of an atom or molecule. Process (2) is the inverse of process (1) and is also known as a second-kind collision.

8.3. BASIC CHARACTERIZATION OF ELECTRONS

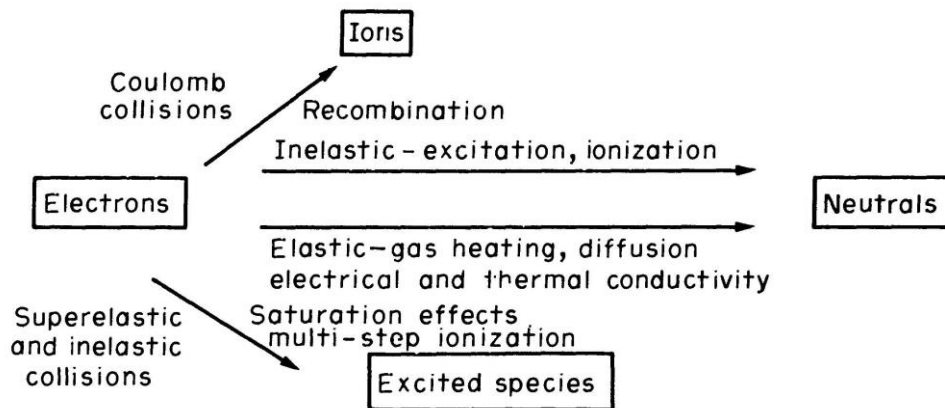


Figure 9: Important electron collisional interactions from [51]

The electron density parameter is easy, and it is directly proportional to the electric current across the medium in most gas discharges. Furthermore, as previously mentioned, the quasi-neutrality criterion necessitates about equal concentrations of positive and negative charge.

The electron temperature parameter is a result of the electron gas's "statistical" character. Because of the huge number of particles involved, electrons are classified as a gas with classical Maxwell-Boltzmann statistics governing its statistical structure. The Maxwellian distribution describes the distribution of electron velocities (or energies) in thermodynamic equilibrium, allowing an electron temperature, T_e , to be set so that the mean electron energy is proportional to T_e :

$$m \langle v^2 \rangle / 2 = 3k T_e / 2 \quad (1)$$

Where v^2 is the mean square electron velocity (v is the electron velocity, which is mostly the thermal or random velocity of the electrons), k is Boltzmann's constant, m is the electron mass, and T_e is the electron temperature in degrees Kelvin.

Debye Shielding

Assume we begin with a uniformly charged neutral medium into which a positive point test charge $+Q$ is inserted. In empty space, we know that the test charge's Coulomb potential is

$$v(r) = \frac{Q}{4\pi\epsilon_0 r} \quad (2)$$

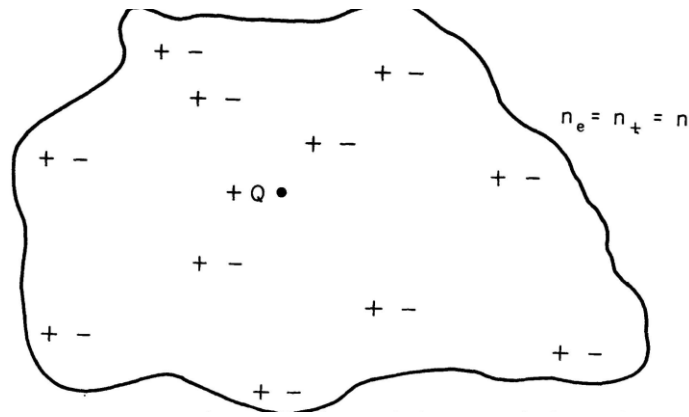


Figure 10: Ionized medium with a positive charge perturbation from [51]

This describes the positive charge's impact zone in free space, or how far into the medium an external effect may be perceived. The field will not be exactly Coulombic in the ionized medium because the electrons will prefer to migrate towards the test charge while the ions will move away. The test charge will be neutralized or "shielded" from the remainder of the medium as a result of this.

Plasma Frequency

Charge screening describes how electrons and ions shift their locations to counteract the effects of a charge disturbance. The issue now is how soon this can happen. This will give you a sense of how a plasma behaves dynamically. This question may be investigated in two ways. We employ the most basic imaginable model of an ionized gas in both cases. We'll suppose that all charged particles are cold, meaning that they don't have any thermal motion. Only the directed motion of electrons will be considered, and we will assume that the motion of one electron (or ion) is representative of the movements of all electrons.

We will first perturb the density of a plasma and then compute the restoring force and the natural frequency of oscillation in the initial approach to the plasma frequency.

The plasma frequency's physical relevance may be deduced from the formalism that contains it. If $\omega > \omega_p$, the relative dielectric constant is positive and smaller than 1, assuming the electron gas is a dielectric. As a result, an electromagnetic wave with frequency ω may travel across the electron plasma. The perturbation changes faster than the plasma can shelter it, allowing it to permeate the electron gas. The relative dielectric constant is negative if $\omega < \omega_p$. In terms of a dielectric, this implies that an electromagnetic wave will not be able to pass through the electron gas. In terms of physics, the plasma may react rapidly enough to protect the electron gas from the electromagnetic disturbance. At this frequency in the plasma, self-sustained oscillations may occur, which is compatible with the prior method of estimating the plasma frequency.

9. ELEMENTARY THEORY OF A GAS DISCHARGE

The electrons were considered to have no random velocity and no interactions with themselves or other species inside the medium when the plasma frequency was calculated. The first assumption is obviously incorrect; but, if we just examine the average directed velocity of electrons under the influence of an external field, the random movements cancel out, thus we may continue to ignore the random motion until a comprehensive kinetic theory method is established. If we want to proceed beyond a basic equation for the dielectric constant of an electron plasma, we must begin to consider particle interactions on a fundamental level.

9.1. THE LANGEVIN EQUATION

The Lorentz gas is the most basic model that contains interactions. The electrons are free to move in this model against a motionless homogeneous backdrop of ions and neutrals, which provides a viscous damping force. The space charge fields are thought to be the sole means by which electrons interact with one another.

Fortunately, this is a suitable representation of the medium we're interested in: one that's weakly ionized and dominated by electron-neutral collisions. We keep Newton's equations to explain the external forces acting on the electron, but we add a term to account for the electrons' momentum loss owing to collisions with background ions and neutrals. This term is included in the Langevin equation, which is as follows:

$$\frac{d}{dt} m\bar{u} = -e [\bar{E} + \bar{u} \times \bar{B}] - m\bar{u} v_m \quad (3)$$

The collision frequency for momentum transfer is specified by v_m . This indicates that the electron loses all of its directed motion on average v_m times per second. Figure depicts a model of a billiard ball collision in which an electron loses all of its momentum.

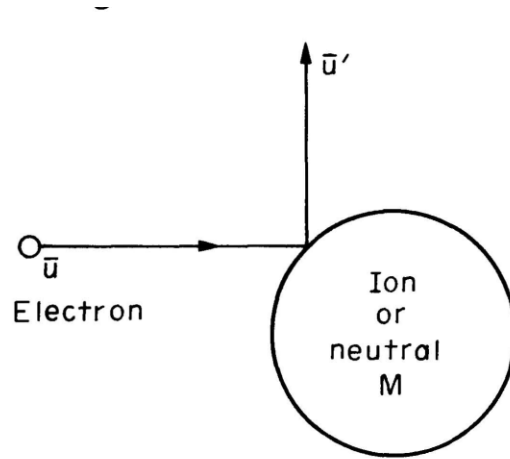


Figure 11: A model of a collision in which an electron loses all its momentum from [51]

In this collision, all motion in the x direction is lost, but the magnitude of the electron velocity (energy) stays unchanged, save for a tiny percentage that is lost in the ion or neutral's recoil. If the ions or neutrals remain immobile, a proportion $\delta = 2m/M$ of the initial electron energy ($m\langle v^2 \rangle/2$) is lost in such an elastic collision, as will be illustrated later.

The directed velocity of an "average" electron, which is supposed to be typical of all the electrons in the discharge, is obtained by solving equation. After multiplying the findings for one electron by the density of electrons, the result is considered to represent the whole gas discharge. Only if v_m is independent of electron velocity, as will be demonstrated later, is this method strictly accurate.

9.2. MOBILITY, CONDUCTIVITY AND DIELECTRIC CONSTANT

The magnetic field may be disregarded at first, and the electric field can be thought of as oscillatory.

$$\bar{E} = \bar{E}_0 e^{j\omega t} \quad (4)$$

The entire Langevin equation may be used to calculate the conductivity of a magneto-ionic medium.

$$(v_m + j\omega)m\bar{u} = -e\bar{E} - e\bar{u} \times \bar{B}_0 \quad (5)$$

The ion terms play a different function in the magneto-ionic medium than the electron terms, therefore the extra ion terms in the conductivity or dielectric constant (which are simply added to the electron terms) may be derived by replacing the electron terms.

$$\Omega_p^2 = \frac{m}{M} \omega_p^2 \text{ for } \omega_p^2$$

$$-\Omega_c = \frac{-e B_0}{M} \text{ for } \omega_c \quad (6)$$

The state in which the velocity of the electron in the magnetic field is in synchronism with the driving electromagnetic field, setting up a scenario in which the electron continually acquires energy from the electric field, is known as the conductivity peak. This is similar to the circumstances seen in a DC field, where collisions slow down the electrons' (or current's) velocity ($\text{Re } \sigma \frac{1}{v_m}$), limiting the amount of energy absorbed.

10. COLLISIONS

We characterized the interaction of electrons (or other particles) with the other elements of the plasma in terms of a "collision frequency for momentum transfer," which indicates the viscous loss in the medium, in our explanation of the Langevin equation and its applications. We need to be able to calculate v_m for the gas components in issue for specific applications of the Langevin equation. We need to delve at the more basic characteristics of collisions in plasmas since v_m will be affected by the species with which the electrons (or other particles) clash, the density of the collision partners, and the relative velocities of the colliding particles. When studying the more precise theory (Boltzmann equation) of gas discharges, we must also understand some of the collisional interactions in more depth. As a result, at this point, we'll attempt to connect some of these fundamental ideas.

The collision frequency will be related to the collision cross section a , and then to the differential scattering cross section, $d\sigma/d\Omega$, which comprises the basic characteristics of the collisional interaction between two particles. Schematically,

$$v \leftrightarrow \sigma \leftrightarrow \frac{d\sigma}{d\Omega}$$

10.1. CROSS SECTION, MEAN FREE PATH AND COLLISION FREQUENCY

Let's start with the collision section a , which is a basic quantity. If we imagine an atom to be effectively a "billiard ball" with a radius of a , an electron traveling towards this atom will collide if its trajectory falls inside the "shadow" of the billiard ball. For this basic model, the collision cross section is the area hidden by the atom, or $\sigma = \pi a^2$.

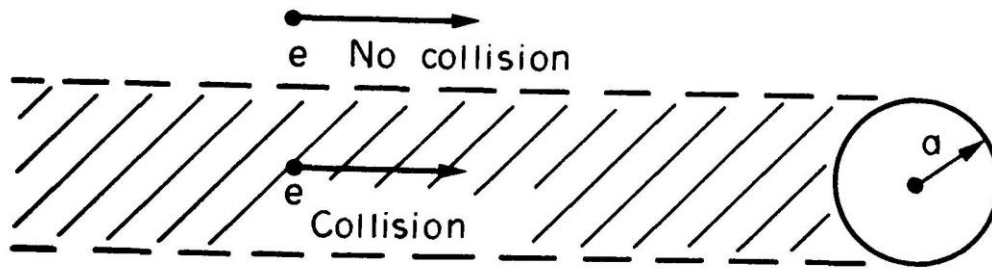


Figure 12: Concept of collision cross section from [51]

The fact that electron-molecule collisions are not simple billiard ball collisions, but instead reflect an interaction between the entering electrons and the electrons plus the nucleus of the molecule, explains why the cross section is dependent on electron velocity (or energy). As a result, the electron and the molecule have a spatially variable interaction potential, which causes the cross section to fluctuate with the relative velocities of the two collision partners, as will be observed later. The sum of the drift velocity and the random or thermal velocity is the total electron velocity. In most circumstances, the velocity used to determine σ is just the electron's thermal velocity. We may use our basic concept of a cross section being about the area of the collision partner to get some preliminary estimates of the magnitudes of σ . We're talking about areas of $\approx 10^{-19} \text{m}^2$ for atoms, plus or minus a few orders of magnitude. We'll show several charts of σ as a function of electron energy for different gases in AB instances (assuming elastic collisions only).

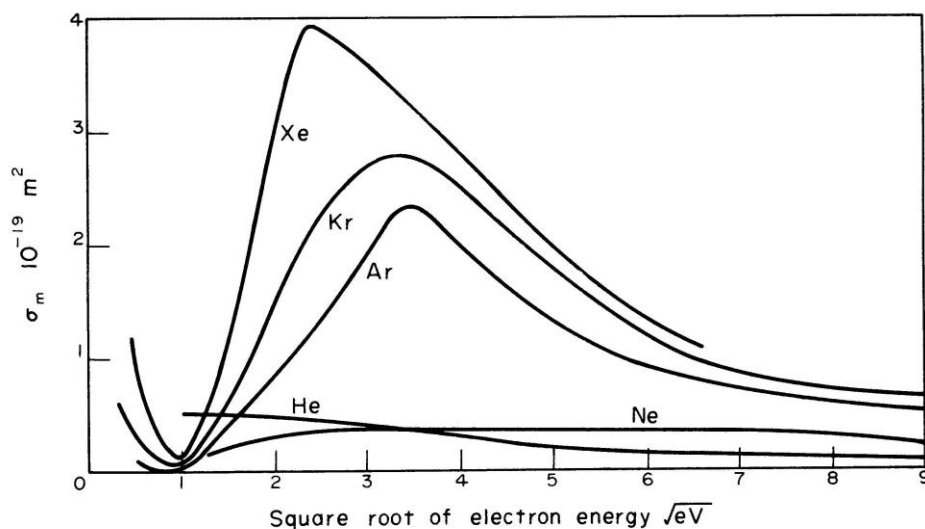


Figure 13: Elastic collision cross sections for the rare gases from [51]

10.2. CLASSICAL SCATTERING BY A CENTRAL FORCE

We're going to look at how a central force scatters a particle. That is, the scattering partner's potential is entirely radial (spherically symmetric) $v = V(r)$. There may be angular dependences of V in general, but this complicates the solutions and is probably best addressed via quantum theory, which explicitly treats the angular momentum of quantum states of atoms. We'll look at scattering in a system where the scattering centre is assumed to be stationary (the Laboratory coordinate system),

In general, we can solve for $c(v)$ and b if $V(r)$ is known.

An perfect analytical answer can be discovered in just a few circumstances. If we suppose $V(r)$ to be of the form described by Goldstein (1959)

$$V(r) = ar^n \quad (1)$$

In terms of circular functions, accurate solutions may be determined for $n = 2, -1, -2$, and $n = 6, 4, 1, -3, -4, -6$ in terms of elliptic functions. Elliptic solutions may also be found with certain fractional exponents. Let us now apply this approach to two gas discharge scenarios that are extremely fascinating.

10.3. INELASTIC COLLISIONS

The majority of collisions examined so far have been "elastic" collisions, in which the collision partners' internal energy is basically unaffected.

These collisions are crucial in defining the electrical and thermal conductivities, diffusion coefficients, mobilities, and other transport coefficients in a gas. The "inelastic collisions," which are critical in determining such key discharge parameters as the electron temperature or energy, the electron number density, and the populations of the many excited species within the gas, are, in many respects, the most significant class of collisions. There are massive energy exchanges between the collision partners in these collisions, resulting in a change in the collision partners' internal energy. Many sorts of processes are covered in the introduction. The four-volume second edition of *Electronic and Ionic Impact Phenomena* has an outstanding compilation of material on these collisional phenomena.

Attachment

An electron may be caught by a neutral to generate a negative ion in electronegative gases. The particular mechanisms may be intricate, but they usually involve the production of an unstable

molecular negative ion, which then dissociates. As a consequence, electron energy may have a big impact on cross section. Some used electron impact to establish the cross sections for the production of o^- from o^2 , co , and co_2 and discovered the cross sections for the generation of negative ions in water vapor in a similar way. The cross sections that have been supplied so far have mostly been used to demonstrate processes. Many other important processes, such as vibrational-vibrational energy exchange collisions or vibrational-rotational energy exchange collisions in molecules, are also important. However, these processes are often described in terms of collision or response rates (one of which is the collision frequency for momentum transfer). To think about reaction rates, you need to know how the energy of the particles involved in the reaction are distributed. After considering the idea of the distribution function, all subsequent collision processes will be referred to when the requirement arises.

11. DISTRIBUTION FUNCTIONS AND BOLTZMANN EQUATION

11.1. Collisional Rates for a Maxwellian Distribution

Of fact, a perfectly Maxwellian distribution is unlikely, since it would rule out any current flow in the discharge, for example. However, since electron distribution functions are often found to be extremely near to Maxwellian, this form may be utilized to determine several essential collisional rates.

$$\langle \sigma(v)v \rangle = \frac{1}{n} \int_0^\infty \sigma(v)f(v) dv = 4\pi \left(\frac{m}{2\pi KT} \right)^{3/2} \int_0^\infty v^3 \sigma(v) e^{-mv^2/2KT} dv \quad (1)$$

Because the cross sections are usually stated in terms of the interacting particles' respective energies rather than their relative speeds, rewriting the Maxwellian speed distribution as a Maxwellian energy distribution is simple.

$$f(\epsilon) = \frac{2\sqrt{\epsilon}}{\sqrt{\pi}(KT)^{3/2}} e^{-\epsilon/KT} \quad (2)$$

where $f(\epsilon)$ has been normalized so that

$$\int_0^\infty f(\epsilon)d\epsilon = 1 \quad (3)$$

(ϵ is the energy in joules).

Consider the electron impact excitation of the 6^3P_1 radiating state in mercury as an example of a particular rate calculation. Figure depicts the real cross section. The mean electron energy is generally rather low in mercury discharges, on the order of about 1 eV, so $f(E)$ has the relative

shape shown in Figure. Obviously, only those few electrons in the tail of the distribution do any exciting. For this purpose, the exponential character of the distribution function dominates the slower decay of the excitation cross section, and for simplicity we can approximate the cross section as shown in Figure.

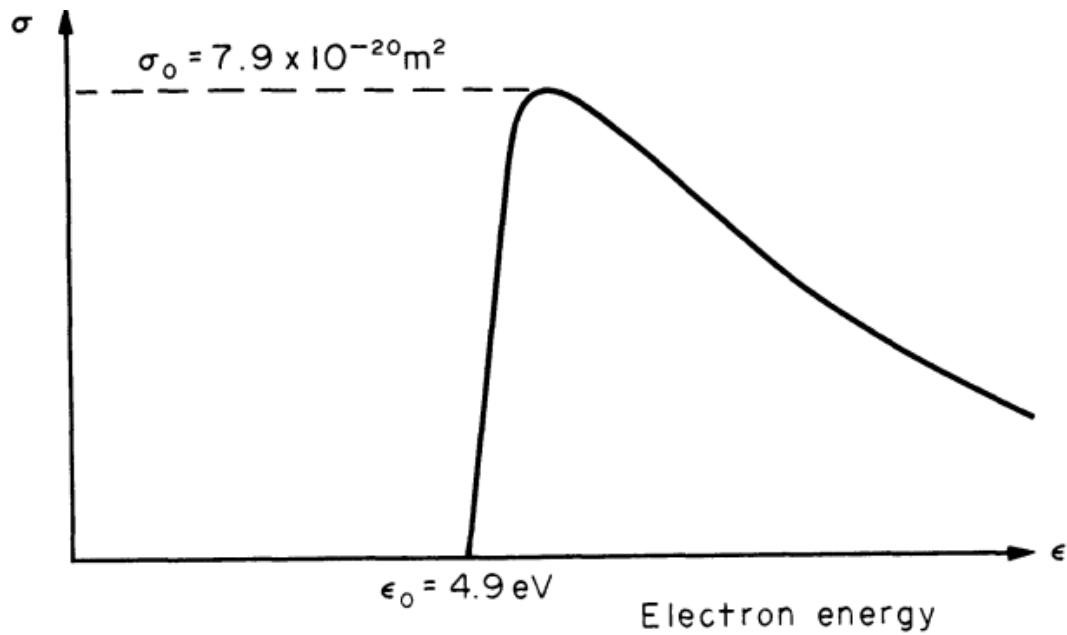


Figure 14: Excitation cross section for the mercury 6^3P_1 state from [51]

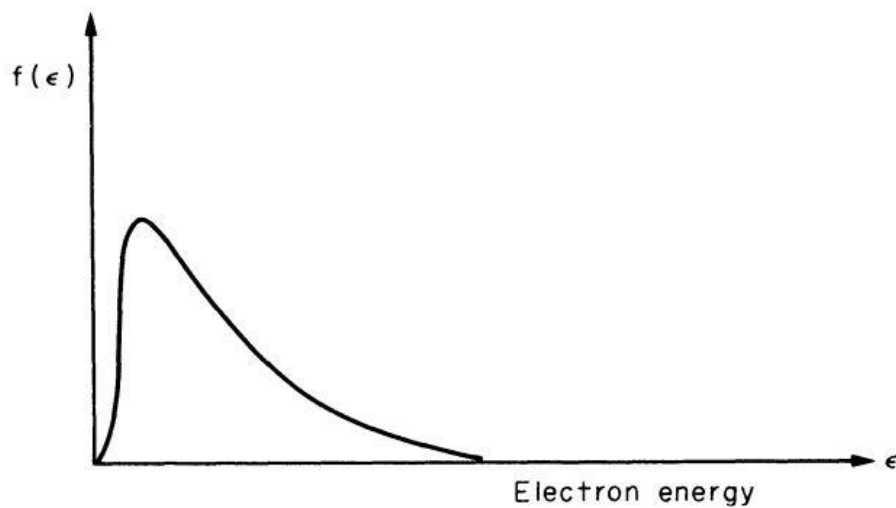


Figure 15: Relative Maxwellian electron energy distribution from [51]

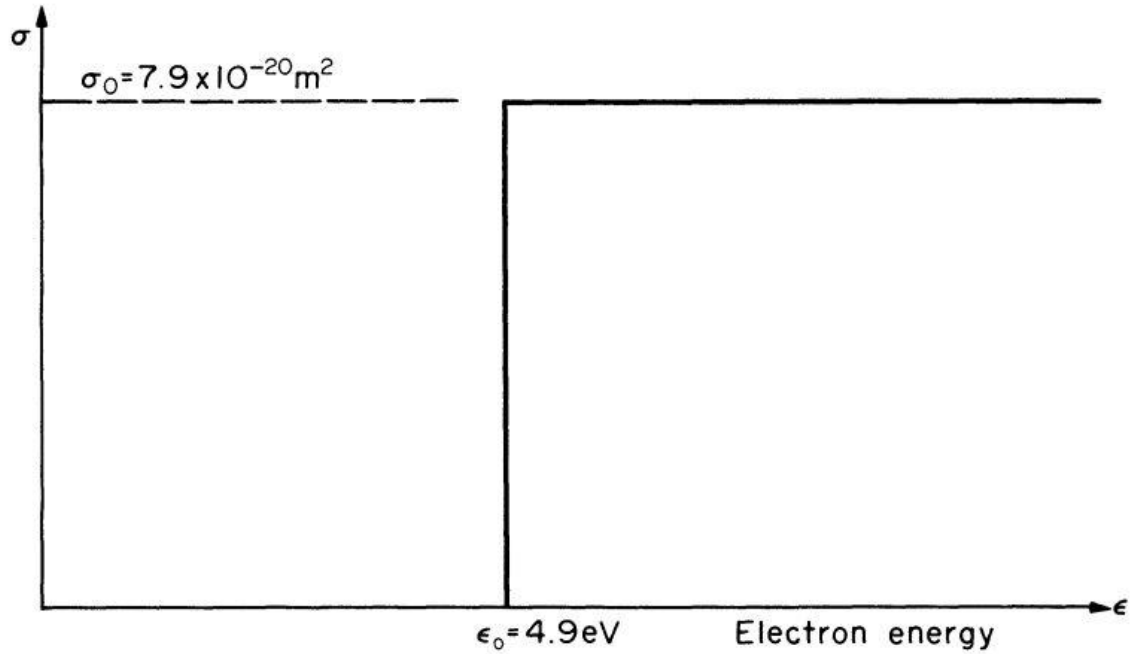


Figure 16: Approximate excitation cross section for the mercury 6^3P_1 state from [51]

The integral equation then becomes

$$\langle \sigma v \rangle = \sigma_0 \int_{\epsilon_0}^{\infty} \frac{2}{\sqrt{\pi}(kT_e)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT_e} \cdot \frac{\sqrt{2\epsilon}}{\sqrt{m}} d\epsilon \quad (4)$$

Which becomes

$$\langle \sigma v \rangle = \left(\frac{8e}{m\pi}\right)^{1/2} \sigma_0 \left(\frac{kT_e}{e}\right)^{1/2} \left[1 + \frac{\epsilon_0}{kT_e}\right] e^{-\epsilon_0/kT_e}. \quad (5)$$

In this expression, ϵ_0 is in joules and kT_e/e is in volts. As in most integrations, this function is a relatively smooth function of mean electron energy (kT_e) even though σ is a sharp function of ϵ . The resultant $\langle \sigma v \rangle$ (m^3/sec) as a function of kT_e/e (volts) is shown in Figure. A further examination of equilibrium distributions also allows us to calculate the rates for inverse processes with only the knowledge of the cross section or rate for the direct process by invoking the principle of detailed balance.

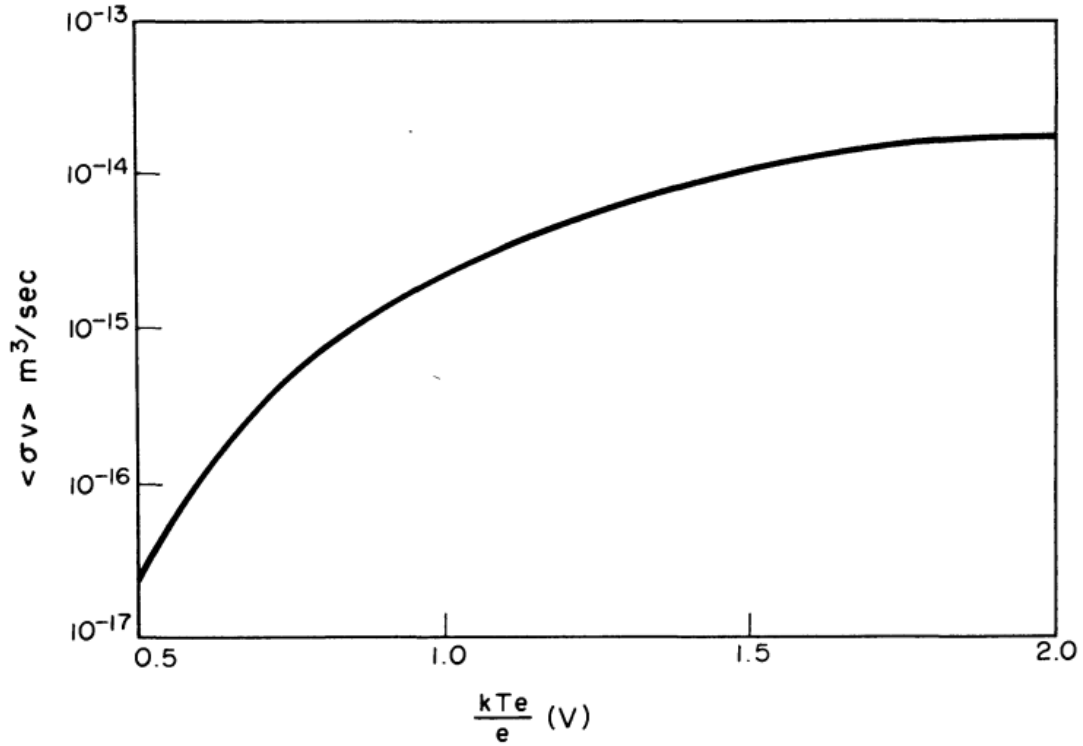


Figure 17: Excitation rate as a function of characteristic electron energy from the equation (5) from [51]

11.2. DETAILED BALANCE AND INVERSE PROCESS

The energy distributions of all free particles and the populations of all stimulated species are known if a system is in thermodynamic equilibrium. This isn't a very fascinating condition in and of itself, but it enables us to identify the link between any given process (say, collisional excitation) in a gas discharge and its inverse (collisional de-excitation) by simply invoking it. Consider two energy levels of a certain atomic species in a medium, for example. The degeneracies are g_1 and g_0 , and the energy difference between the levels is $\Delta\epsilon$. In thermodynamic equilibrium, we have the Boltzmann distribution.

$$n_1 = n_0 \frac{g_1}{g_2} e^{-\Delta\epsilon/KT_e} \quad (6)$$

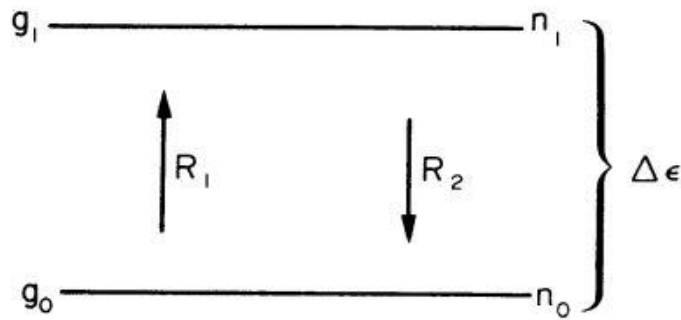


Figure 18: A simple two-level system from [51]

12. AN ATMOSPHERIC PRESSURE HUMID AIR PLASMA KINETIC MODEL

Models that describe the breakdown of gases in electric discharge or electron-beam systems need consistent kinetics data. A central database defining the governing reactions of neutral species in non-thermal low temperature (300-700K) pulsed plasmas containing humid air had been developed, with rate constants and extrapolation methods delivered in such a way that reactivities could be forecasted as a function of temperature and pressure more quickly.

For the controlling reactions of neutral species occurring in humid air plasmas, a suggested database of positive ion-molecule reactions has been created long ago. It's a primary database—a limited subset of critical responses that reveals the system's physical constitution. The figures were derived through a review of the whole literature as well as a comparison of contradictory and relative response rates. The progression from 480 Herron and Green third order to pseudo second-order kinetics was also defined by the estimation methodologies for specific rate constants in the "fall-off" pressure zones. At temperatures up to 600 K and pressures up to 105 Pa, rate constants and extrapolation techniques are presented in a way that aids in the creation of foretelling models of non-thermal plasma chemistry (1 atm). Outside of these pressures, extra reactions must be considered, notably association reactions, which complicate excited-state chemistry. With a shift in the core set of key reactions, mechanisms change at higher temperatures.

Several mathematical models of Surface Micro Discharge (SMD) in humid air at atmospheric

pressure were developed throughout time. Plasma chemistry model of surface micro discharge in humid air and dynamics of reactive neutral species was tabled, and it included more than 50 species and 600 rudimentary reactions, as well as two coupled well-mixed areas with a discharge layer containing both charged and neutral species and an afterglow region containing only neutral species. Several time phases were included to the model to describe the discharge layer's fast dynamic behaviour and the afterglow's comparably sluggish diffusion and response. After the nozzle exit, chemically reactive H, N, O, and OH radicals are created in large quantities, with H₂, O₂ (1g), O₃, H₂O₂, NO₂, N₂O, HNO₂, and HNO₃ being the most common 'long lasting' species. Their densities range from $2 \cdot 10^{13} \text{ cm}^{-3}$ to $4 \cdot 10^{15} \text{ cm}^{-3}$, corresponding to concentrations of 1 to 200 ppm. In the afterglow zone, O₃ had the greatest density (2%), indicating that O₃ was important in a variety of biological applications under the circumstances studied. Furthermore, HNO₃ may be useful in the treatment of aqueous media. Because HNO₃ is a strong acid (p K_a 1.4), the pH in the gas phase lowers owing to plasma-generated nitric acid. High O, H, and N densities in the jet are often seen as a result of ppm contaminants in the gas input being partly produced inside the device. Furthermore, ambient air diffusion begins to significantly stimulate all density profiles from 0.25 cm behind the nozzle exit. Atomic oxygen has the highest density at 0.8 cm ($8 \cdot 10^{15} \text{ cm}^{-3}$) and then begins to fall as this species (primarily) correlates with O₂ to produce ozone and evolves into the dominant species in the effluent ($5 \cdot 10^{15} \text{ cm}^{-3}$), where power density and gas temperature are rapidly decreasing. The other radicals (N, H, and OH) are fulfilled more efficiently than O, and they are largely transformed into HO₂ and NO. Dissociative attachment of oxygen and water molecules produces negatively charged species. The results are qualitatively consistent with infrared absorption spectroscopy using the Fourier transform. Even after 15 minutes of SMD exposure, simulation findings indicated that the density of reactive species continued to increase dramatically over time. The findings show that SMD treatments lasting a few minutes or fewer involve significant neutral species concentration and flux transients, which might alter comprehension of the results.

A mathematical model of SMD was constructed to examine plasma chemistry in humid air at room temperature at low power (0.05 W cm^{-2}) using approximately 50 species and 600 elementary reactions. The use of a multiple time-step method between the discharge layer and the afterglow area allowed for decoupling between discharge dynamics and neutral diffusion–response simulations that lasted tens of minutes. The simulation results showed that neutral species disseminations in the afterglow zone are only temporary even after 1000 seconds of

exposure because the sluggish neutral–neutral interaction is the procedure's limiting element. The dynamic behaviour of neutrals is rather important in real-world situations. Our modelling results reveal that when SMD is employed for surface sterilization, the flow of reactive species onto bacterium cells alters over time. Because the Treated cells may be exposed to a variety of reactive species during SMD treatment, care must be taken to infer the biological effect. Because the rate of mass transfer is limited by relatively slow gas-phase diffusion, simulation of highly reactive species is often fulfilled in the discharge layer. Furthermore, it was discovered that a sufficient change in device design might aid reactive species in reaching the treated surface. When the distance between the SMD and the treated surface is adjusted to 1 mm instead of 10 mm, a convective flow of 10 m s⁻¹ is created, and the usual mass transfer time is decreased to only 0.1 ms. As we lack comprehensive understanding on the issue, many novel phenomena will be discovered in the future, such as the complexity and nonlinearity of atmospheric pressure and multiphase plasma systems.

The plasma chemistry in an argon plasma jet flowing into humid air is described using a zero-dimensional, semi-empirical model. The model produces species density profiles as a function of position in the plasma jet device and run-off. A reaction chemistry creates an argon/humid air combination that can accommodate a variety of species and reactions, making it helpful for higher-level computational models. O₂ and later in the effluent NO₃ prevail over the other anions due to association or charge transfer interactions with neutrals. Water clustering of positive ions is particularly important under certain situations, according to simulations. The impact of altering gas temperature, flow speed, power density, and air humidity on chemistry is being investigated, as well as the effects of vibrational excitation on the predicted electron temperature

The time-dependent development of species densities in the 0D chemical kinetics model is modified to a spatial dependency owing to the function of location in the plasma jet device and run-off in the 0D chemical kinetics model. The argon feed gas is released into the outside air. The argon excimer, Ar₂^{*}, is created by association reactions of argon meta stables with the background gas, and free electrons are mainly created by electron-impact ionization of the argon excimer, Ar₂^{*}. When argon species travel through humid ambient air, they are chemically satisfied by the air molecules, resulting in the formation of atomic species. The rapid decrease in electron density from 0.3 cm beyond the nozzle exit is also due to dissociative attachment procedures. Furthermore, the anion densities might be affected by the formation of negative clusters. Positive ions are produced primarily by charge transfer with argon ions, but

they are quickly converted to H_3O^+ (H_2O)_x water clusters. Elastic collision losses with Ar have been shown to be the largest when the electron density is high, and air is only present in ppm amounts. The biggest contributions come from electronic excitation of nitrogen, vibrational excitation of nitrogen, and electronic excitation of argon atoms. As a result, the vibrational states must be considered in order to establish the electron temperature as precisely as feasible. Furthermore, changing the experimental circumstances, such as gas temperature, gas flow speed, power density, and air humidity, reveals effects that are specific to each species, varied in each condition, and readily quite substantial. As a result, by altering the environment, it is possible to favor the development of certain species or groups of species, such as NOx molecules. However, due to the short time scales, it will be difficult to completely remove some species unless the composition of the surrounding environment is regulated.

Mathematical simulations are used to examine the mechanism of air ionization by a single millisecond discharge under atmospheric circumstances. ZDPlasKin is used to describe plasma kinetics, while BOLSIG+ is used to determine the electron energy distribution function. For $n_e > 10^{16} \text{ cm}^{-3}$, the model incorporates the excited electronic states of O and N atoms, which are demonstrated to play a major role in plasma ionization. A non-equilibrium plasma ($T_e > T_{\text{gas}}$) is generated at ambient circumstances with electric fields typical of nanosecond discharges, with leftovers partially ionized for around 12 nanoseconds ($n_e 10^{16} \text{ cm}^{-3}$). The discharge then abruptly achieves full ionization ($n_e = 10^{19} \text{ cm}^{-3}$) and thermalization ($T_e = T_{\text{gas}} 3 \text{ eV}$) in less than half a nanosecond, as observed in experiments. The electron impact ionization of atomic excited states explains the fast ionization process, whereas elastic electron-ion collisions cause the fast thermalization.

With 0D simulations using ZDPlasKin and BOLSIG+, the mechanism of ionization in ambient air by a 15 ns pulse of 47 kV/cm was investigated. The electron-impact ionization of N₂ and O₂ dominates the electron generation phase at first. The density of atomic species rises as molecules dissociate. Electron-impact excitation populates the excited electronic states of atoms and molecules. The simulations show that the ionization of N excited states dominates the ionization of N₂ for $n_e > 10^{16} \text{ cm}^{-3}$ (X, A, B, a, C). In less than half a millisecond, the electron number density jumps by two orders of magnitude (from 10^{17} cm^{-3} to more than 10^{19} cm^{-3}). This behaviour cannot be replicated by ignoring the ionization of the electronic excited states of O and N. Due to electron-ion elastic collisions, the gas temperature rises from 300 to 37 000 K at the same time. When the plasma is completely ionized, the EEDF is discovered to be Maxwellian.

GOALS:

Building a database of kinetic reactions with rate coefficients ready for implementation in the ZDPlasKin software

MODEL FROM PARK:

Reaction No	Reactants	Products	Rate coefficient (K)
1	O + O + M	O ₂ + M	$3.2\text{D-}47 \cdot \exp(9.0\text{D}2/T_{\text{gas}})$
2	O + O ₂ + M	O ₃ + M	$3.4\text{D-}46 \cdot (3.0\text{D}3/T_{\text{gas}})^{**}1.2\text{d}0$
3	O + O ₃	O ₂ + O ₂	$8.0\text{D-}18 \cdot \exp(-2.06\text{D}3/T_{\text{gas}})$
4	O + NO + M	NO ₂ + M	$1.0\text{D-}43 \cdot (3.0\text{D}3/T_{\text{gas}})^{**}1.6\text{d}0$
5	O + NO	NO ₂	$3.01\text{D-}17 \cdot (T_{\text{gas}}/2.98\text{D}2)^{**}0.3\text{d}0$
6	O + NO ₂	NO + O ₂	$5.5\text{D-}18 \cdot \exp(1.92\text{D}2/T_{\text{gas}})$
7	O + NO ₂ + M	NO ₃ + M	$1.31\text{D-}43 \cdot (2.98\text{D}2/T_{\text{gas}})^{**}1.5\text{d}0$
8	O + NO ₂	NO ₃	$2.3\text{D-}17 \cdot (T_{\text{gas}}/2.98\text{D}2)^{**}0.2\text{d}0$
9	O + NO ₃	O ₂ + NO ₂	1.7D-17
10	O + N ₂ (A ₃ Σ)	NO + N(2D)	7.0D-18
11	O + N ₂ (v)	NO + N	1.0D-17
12	N + N + M	N ₂ + M	$8.3\text{D-}46 \cdot \exp(5.0\text{D}2/T_{\text{gas}})$
13	N + NO	N ₂ + O	$2.1\text{D-}17 \cdot \exp(1.0\text{D}2/T_{\text{gas}})$
14	N + NO ₂	N ₂ O + O	$5.8\text{D-}18 \cdot \exp(2.2\text{D}2/T_{\text{gas}})$
15	N + NO ₂	N ₂ + O + O	9.1D-19
16	N + NO ₂	NO + NO	6.0D-19
17	N + NO ₂	N ₂ + O ₂	7.0D-19
18	N + O + M	NO + M	$6.3\text{D-}45 \cdot \exp(1.4\text{D}2/T_{\text{gas}})$
19	N + O ₂	NO + O	$4.47\text{D-}18 \cdot (T_{\text{gas}}/2.98\text{D}2)^{**} \exp(-3.27\text{D}3/T_{\text{gas}})$
20	N + O ₃	NO + O ₂	5.0D-22
21	O ₃ + NO	NO ₂ + O ₂	$1.8\text{D-}18 \cdot \exp(-1.37\text{D}3/T_{\text{gas}})$
22	O ₃ + NO ₂	NO ₃ + O ₂	$1.2\text{D-}19 \cdot \exp(-2.45\text{D}3/T_{\text{gas}})$
23	O ₃ + M	O + O ₂ + M	$3.92\text{D-}16 \cdot \exp(-1.14\text{D}4/T_{\text{gas}})$
24	O ₃ + O ₂ (a ₁ Δ)	O + O ₂ + O ₂	$5.2\text{D-}17 \cdot \exp(-2.84\text{D}3/T_{\text{gas}})$
25	NO + NO ₂ + M	N ₂ O ₃ + M	$3.09\text{D-}46 \cdot (3.0\text{D}2/T_{\text{gas}})^{**}7.7\text{d}0$
26	NO + NO ₃	NO ₂ + NO ₂	$1.8\text{D-}17 \cdot \exp(1.1\text{D}2/T_{\text{gas}})$
27	NO ₂ + NO ₂ + M	N ₂ O ₄ + M	$1.44\text{D-}45 \cdot (2.98\text{D}2/T_{\text{gas}})^{**}3.8\text{d}0$
28	NO ₂ + NO ₃ + M	N ₂ O ₅ + M	$3.7\text{D-}42 \cdot (2.98\text{D}2/T_{\text{gas}})^{**}4.1\text{d}0$
29	NO ₂ + NO ₃	NO ₂ + NO ₂ + O ₂	$2.3\text{D-}19 \cdot \exp(-16\text{D}2/T_{\text{gas}})$
30	NO ₃ + NO ₃	NO ₂ + NO ₂ + O ₂	$8.5\text{D-}19 \cdot \exp(-2.45\text{D}3/T_{\text{gas}})$

31	N ₂ O ₃ + M	NO + NO ₂ + M	1.09D-16*exp(-2.628D3/Tgas)
32	N ₂ O ₄ + M	NO ₂ + NO ₂ + M	1.11D-13*exp(4.952D3/Tgas)
33	N ₂ O ₅ + M	NO ₂ + NO ₃ + M	4.92D-11*exp(-1.004D4/Tgas)
34	N ₂ O+ N ₂ (A ₃ Σ)	O + N ₂ + N ₂	8.0D-17
35	N ₂ O+ N ₂ (A ₃ Σ)	NO + N+ N ₂	8.0D-17
36	NO ₂ + N ₂ (A ₃ Σ)	N ₂ + NO + O	1.3D-17

Reaction No	COMMENTS
1	Herron and Green 2001 p. 468 Table II Ox reaction Equation 1: $K=4.5E-46*\exp(630.0/T_{gas})$
2	Herron and Green 2001 p. 468 Table II Ox reaction Equation 3 and 4: $K=6.0E-46*(T_{gas}/300)^{-2.85}[O_2]$ $K=6e-46(T_{gas}/300)^{-2.85}[N_2]$
3	Herron and Green 2001 p. 465 Table I O Reaction Equation 1
4	Herron and Green 2001 p. 468 Table II Nox reaction Equation 1
5	Capitelli, Ferreira, Gordiets, Osipov 2000 p.168 Table 10.1 R10 : $O+NO\rightarrow NO_2+ hv$ $K=4.2E-18$
6	Atkinson, Baulch, Cox, Crowley, Hampson, Hynes, Jenkin, Rossi, Troe 1992 p.1463 Table 1 R32
7	Atkinson, Baulch, Cox, Crowley, Hampson, Hynes, Jenkin, Rossi, Troe 1992 p.1463 Table 1 R33
8	Atkinson, Baulch, Cox, Crowley, Hampson, Hynes, Jenkin, Rossi, Troe 1992 p.1463 Table 1 R34: $O+NO_3\rightarrow NO_2+O_2$ $k=1.7E-11$
9	Herron and Green 2001 p. 465 Table I O Reaction Equation 3
10	Atkinson, Baulch, Cox, Hampson, Kerr, Rossi, Troe 1992 No equation is available
11	Atkinson, Baulch, Cox, Hampson, Kerr, Rossi, Troe 1992 No equation is available
12	Atkinson, Baulch, Cox, Hampson, Kerr, Rossi, Troe 1992 No equation is available
13	Herron and Green 2001 p. 465 Table I N Reaction Equation 3
14	Herron and Green 2001 p. 465 Table I N reaction Equation 4
15	O. Eichwald, M. Yousfi, A. Hennad, M.D. Benabdessadok 1992 pg.4793 Table 7 4th equation
16	O. Eichwald, M. Yousfi, A. Hennad, M.D. Benabdessadok 1992 pg.4793 Table 7 5th equation
17	O. Eichwald, M. Yousfi, A. Hennad, M.D. Benabdessadok 1992 pg.4793 Table 7 3rd equation $K=9.1E-13$
18	Herron and Green 2001 p. 468 Table II Ox reaction Equation 2
19	Baulch, Cobos, Cox, Frank, Hayman, Just, Kerr, Murrells, Pilling, Troe, Walker, Warnatz (1994) pg.950 Preferred Value $K=1.5E-20*T_{gas}*\exp(-3270/T_{gas})$

20	O. Eichwald, M. Yousfi, A. Hennad, M.D. Benabdessadok 1992 pg4794 Table 7 3rd equation
21	Herron and Green 2001 p. 466 Table I Nox reaction Equation 1
22	Atkinson, Baulch, Cox, Hampson, Kerr, Troe (1992) pg1129 Table 2 R1198
23	Jeong, Park, Henins, Babayan, Tu, Selwyn, Ding, Hicks p.8030 Table 1 R4:K=7.26E-10*exp(-11400/Tgas)
24	Herron and Green 2001 p. 472 Table III O2(a1Δ) reaction Equation 6
25	Atkinson, Baulch, Cox, Crowley, Hampson, Hynes, Jenkin, Rossi, Troe p.1576 Preferred value
26	Herron and Green 2001 p. 466 Table I Nox reaction Equation 2
27	Atkinson, Baulch, Cox, Crowley, Hampson, Hynes, Jenkin, Rossi, Troe p.1584 Preferred value
28	Atkinson, Baulch, Cox, Crowley, Hampson, Hynes, Jenkin, Rossi, Troe p.1588 Table 1 Preferred value
29	Atkinson, Baulch, Cox, Crowley, Hampson, Hynes, Jenkin, Rossi, Troe p.1616 No equation
30	Johnston, Cantrell and Calvert pg.5159 Abstract 23rd line
31	Atkinson, Baulch, Cox, Crowley, Hampson, Hynes, Jenkin, Rossi, Troe p.1578 Preferred Value $K=1.9E-19*(T_{gas}/300)^{-3.8} \exp(-4880/T_{gas})$
32	Atkinson, Baulch, Cox, Crowley, Hampson, Hynes, Jenkin, Rossi, Troe p.1586 Preferred Value: $K=1.3E-17*(T_{gas}/300)^{-3.8} \exp(-6400/T_{gas})$ $K=1.15E-16 \exp(-6460/T_{gas})$
33	Atkinson, Baulch, Cox, Crowley, Hampson, Hynes, Jenkin, Rossi, Troe p.1591 Preferred Value: $K=1.3E-15*(T_{gas}/300)^{-3.5} \exp(-11000/T_{gas})$
34	Matzing H 2007 pg.391 Table VI No equation
35	Matzing H 2007 pg.391 Table VI No equation
36	Herron and Green 2001 p. 472 Table III N2(A3Σ) reaction 10th Equation

The references to rate coefficients vary from the real material, as stated in the comments.

MODEL FROM SAKIYAMA:

Reaction No	Reactants	Products	Rate coefficient (K)
1	e + N ⁺ + M	N + M	3.12D-35/Te**1.5d0
2	e + N2 ⁺	N + N	1.66D-12/Te** 0.7d0
3	e + N2 ⁺	N(2D) + N	1.5D-12/Te** 0.7d0
4	e + N2 ⁺ + M	N2 + M	3.12D-35/Te** 1.5d0
5	e + N3 ⁺	N2 + N	3.46D-12/Te** 0.5d0
6	e + N4 ⁺	N2 + N2	4.73D-11/Te**0.53d0
7	e + O ⁺ + M	O + M	3.12D-35/Te**1.5d0
8	e + O2 ⁺	O + O	1.68D-11/Te**0.7d0
9	e + O2 ⁺	O + O(1D)	1.24D-11/Te**0.7d0
10	e + O2 ⁺ + M	O2 + M	3.12D-35/Te**1.5d0
11	e + O4 ⁺	O2 + O2	2.42D-11/Te**0.5d0
12	e + N2O ⁺	N2 + O	3.46D-12/Te**0.5d0

13	$e + \text{NO}^+$	$\text{N} + \text{O}$	$1.07\text{D}-11/\text{Te}^{**}0.85\text{d}0$
14	$e + \text{NO}^+$	$\text{N}(2\text{D}) + \text{O}$	$4.28\text{D}-11/\text{Te}^{**}0.85\text{d}0$
16	$e + \text{NO}^+ + \text{M}$	$\text{NO} + \text{M}$	$3.12\text{D}-35/\text{Te}^{**}1.5\text{d}0$
17	$e + \text{NO}_2^+$	$\text{NO} + \text{O}$	$3.46\text{D}-12/\text{Te}^{**} 0.5\text{d}0$
18	$e + \text{H}_2^+$	$\text{H} + \text{H}$	$1.86\text{D}-13/\text{Te}^{**}0.43\text{d}0$
19	$e + \text{H}_3^+$	$\text{H} + \text{H}_2$	$5.20\text{D}-11/\text{Te}^{**}0.5\text{d}0$
20	$e + \text{H}_3^+$	$\text{H} + \text{H} + \text{H}$	$1.14\text{D}-11/\text{Te}^{**} 0.97\text{d}0$
21	$e + \text{H}_2\text{O}^+$	$\text{OH} + \text{H}$	$2.73\text{D}-12/\text{Te}^{**}0.5\text{d}0$
22	$e + \text{H}_2\text{O}^+$	$\text{O} + \text{H}_2$	$1.37\text{D}-12/\text{Te}^{**}0.5\text{d}0$
23	$e + \text{H}_2\text{O}^+$	$\text{O} + \text{H} + \text{H}$	$1.37\text{D}-12/\text{Te}^{**}0.5\text{d}0$
24	$e + \text{H}_3\text{O}^+$	$\text{OH} + \text{H} + \text{H}$	$5.46\text{D}-12/\text{Te}^{**}0.5\text{d}0$
25	$e + \text{O}_2 + \text{O}_2$	$\text{O}_2^- + \text{O}_2$	$1.4\text{D}-41*(\text{Tg}/\text{Te})^*\exp(-6.0\text{D}3/\text{Tg})^*\exp\{7.0\text{D}3(\text{Te}-\text{Tg})/(\text{Te}*\text{Tg})\}$
26	$e + \text{O}_2 + \text{N}_2$	$\text{O}_2^- + \text{N}_2$	$1.1\text{D}-43*(\text{Tg}/\text{Te})^{**}2^*\exp(-7.0\text{D}2/\text{Tg})^*\exp\{1.5\text{D}3(\text{Te}-\text{Tg})/(\text{Te}*\text{Tg})\}$
27	$\text{O}_2^- + \text{H}$	$\text{HO}_2 + e$	$1.4\text{D}-15$
28	$\text{O}_3^- + \text{O}_2$	$\text{O}_3 + \text{O}_2 + e$	$2.3\text{D}-17*(\text{Tgas}/2.98\text{D}2)^{**}0.2\text{d}0$
29	$\text{NO}^- + \text{M}$	$\text{NO} + \text{M} + e$	$2.40\text{D}-19$
30	$\text{NO}^- + \text{NO}$	$\text{NO} + \text{NO} + e$	$5.0\text{D}-18$
31	$\text{NO}^- + \text{N}_2\text{O}$	$\text{NO} + \text{N}_2\text{O} + e$	$5.1\text{D}-18$
32	$\text{NO}^- + \text{H}_2$	$\text{NO} + \text{H}_2 + e$	$2.3\text{D}-19$
33	$\text{H}^- + \text{O}_2$	$\text{HO}_2 + e$	$1.2\text{D}-15$
34	$\text{OH}^- + \text{O}$	$\text{HO}_2 + e$	$2.0\text{D}-16$
35	$\text{N}^+ + \text{NO}$	$\text{NO}^+ + \text{N}_2$	$4.72\text{D}-16$
36	$\text{N}^+ + \text{NO}$	$\text{N}_2^+ + \text{O}$	$8.33\text{D}-17$
37	$\text{N}^+ + \text{O}_2$	$\text{O}^+ + \text{NO}$	$2.8\text{D}-16$
38	$\text{N}^+ + \text{OH}$	$\text{OH}^+ + \text{N}$	$3.4\text{D}-16$
39	$\text{N}^+ + \text{OH}$	$\text{NO}^+ + \text{H}$	$3.4\text{D}-16$
40	$\text{N}^+ + \text{H}_2\text{O}$	$\text{H}_2\text{O}^+ + \text{N}$	$1.19\text{D}-15$
41	$\text{N}^+ + \text{H}_2\text{O}$	$\text{NO}^+ + \text{H}_2$	$2.1\text{D}-16$
42	$\text{N}_2^+ + \text{NO}$	$\text{NO}^+ + \text{N}_2$	$3.9\text{D}-16$
43	$\text{N}_2^+ + \text{NO}_2$	$\text{NO}^+ + \text{N}_2\text{O}$	$5.0\text{D}-17$
44	$\text{N}_4^+ + \text{N}_2$	$\text{N}_2^+ + \text{N}_2 + \text{N}_2$	$2.1\text{D}-16^*\exp(\text{Tg}/121)$
45	$\text{N}_4^+ + \text{NO}_2$	$\text{NO}_2^+ + \text{N}_2 + \text{N}_2$	$2.5\text{D}-17$

46	$N_4^{++} + NO_2$	$NO^{++} + N_2 + N_2$	$5.0D-17$
47	$N_4^{++} + H_2$	$H_2^{++} + N_2 + N_2$	$3.0D-17 * \exp(-1.8D3/Tg)$
48	$O^{++} + NO$	$O_2^{++} + N$	$3.0D-16$
49	$O^{++} + OH$	$OH^{++} + O$	$3.3D-16$
50	$O^{++} + OH$	$O_2^{++} + H$	$3.6D-16$
51	$O_2^{++} + O_2 + M$	$O_4^{++} + O$	$5.5D-43 * (3.0D2/Tg)^{**2.7}$
52	$O^{-} + NO_2$	$NO_2^{-} + O$	$1.2D-41$
53	$O^{-} + NO_3$	$NO_3^{-} + O$	$3.0D-41$
54	$O_2^{-} + HNO_3$	$NO_3^{-} + HO_2$	$2.8D-16$
55	$O_3^{-} + NO$	$NO_2^{-} + O_2$	$1.0D-17$
56	$N_2O^{++} + NO_2$	$NO^{++} + N_2 + O_2$	$4.29D-16$
57	$N_2O^{++} + NO_2$	$NO_2^{++} + N_2O$	$2.21D-16$
58	$N_2O^{++} + NO_2$	$NO_2^{++} + N_2O$	$4.59D-17$
59	$N_2O^{++} + O_2$	$O_2^{++} + NO_2$	$2.24D-16$
60	$NO_2^{-} + NO$	$NO^{-} + NO_2$	$2.75D-16$
61	$NO_2^{-} + N_2O$	$NO_3^{-} + N_2$	$5.0D-19$
62	$NO_2^{-} + HNO_3$	$NO_3^{-} + HNO_2$	$1.6D-15$
63	$H_2^{++} + O_2$	$O_2^{++} + H_2$	$7.83D-16$
64	$H_2^{++} + H_2O$	$H_3O^{++} + H$	$3.43D-15$
65	$H_2^{++} + H_2O$	$H_2O^{++} + H_2$	$3.86D-15$
66	$OH^{++} + N_2O$	$N_2O^{++} + OH$	$2.13D-16$
67	$OH^{++} + H_2O$	$H_2O^{++} + H$	$1.59D-15$
68	$OH^{++} + H_2O$	$H_3O^{++} + O$	$1.3D-15$
69	$OH^{-} + O_3$	$O_3^{-} + OH$	$9.0D-16$
70	$O_2^{++} + O^{-}$	$O + O + O$	$1.0D-13$
71	$O_2^{++} + NO^{-}$	$NO + O_2$	$2.0D-13 * (3.0D2/Tg)^{**0.5}$
72	$N^{++} + O^{-}$	$O + N$	$2.0D-13 * (3.0D2/Tg)^{**0.5}$

73	$N^+ + O_2^-$	$O_2 + N$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
74	$N^+ + O_3^-$	$O_3 + N$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
75	$N_2^+ + NO^-$	$NO + N_2$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
76	$N_2^+ + NO_2^-$	$NO_2 + N_2$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
77	$N_2^+ + O_2^-$	$O_2 + N_2$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
78	$N_2^+ + O_3^-$	$O_3 + N_2$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
79	$N_2O^+ + N_2O^-$	$N_2O + N_2O$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
80	$N_2O^+ + NO^-$	$NO + N_2O$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
81	$N_2O^+ + NO_2^-$	$NO_2 + N_2O$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
82	$N_2O^+ + NO_3^-$	$NO_3 + N_2O$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
83	$N_2O^+ + O_3^-$	$O_3 + N_2O$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
84	$N_2O^+ + H^-$	$H + N_2O$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
85	$N_2O^+ + OH^-$	$OH + N_2O$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
86	$N_4^+ + O_2^-$ 89	$O_2 + N_2 + N_2$	1.0D-13
87	$NO^+ + NO_2^-$	$NO_2 + NO$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
88	$NO^+ + O^-$	$O + NO$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
89	$NO^+ + O_4^-$	$O_2 + O_2 + NO$	1.0D-13
90	$NO_2^+ + N_2O^-$	$N_2O + NO_2$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
91	$NO_2^+ + NO^-$	$NO + NO_2$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
92	$NO_2^+ + NO_2^-$	$NO_2 + NO_2$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
93	$NO_2^+ + NO_3^-$	$NO_3 + NO_2$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
94	$NO_2^+ + O^-$	$O + NO_2$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
95	$NO_2^+ + O_2^-$	$O_2 + NO_2$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
96	$NO_2^+ + O_3^-$	$O_3 + NO_2$	$2.0D-13^*(3.0D2)/Tg^{**0.5}$
97	$NO_2^+ + O_4^-$	$O_2 + O_2 + NO_2$	1.0D-13
98	$N(2D) + NO$	N_2O	6.0D-17
99	$N_2(A_3\Sigma) + N_2O$	$O + N_2 + N_2$	8.0D-17
100	$N_2(A_3\Sigma) + N_2O$	$NO + N + N_2$	8.0D-17
101	$N_2(A_3\Sigma) + O_2$	$O_2(a_1\Delta) + N_2$	1.0D-18
102	$N_2(A_3\Sigma) + N$	$N + N_2$	5.0D-17
103	$N_2(A_3\Sigma) + O$	$O(1D) + N_2$	2.3D-17

104	O + O2 +M	O3 +M	3.4D-46*(3.0D2/Tg)**1.2
105	O + H +M	OH +M	1.62D-44
106	O + HNO	OH + NO	5.99D-17
107	O + HNO2	NO2 + OH	2D-17*exp(-3.0D3/Tg)
108	O(1D) + O2	O+O2	6.4D-18*exp(6.7D1/Tg)
109	O(1D) + O	O+O	8.0D-18
110	O(1D) + O2(a1Δ)	O+O2	1.0D-17
111	O(1D) + NO	O+NO	4.0D-17
112	O2(a1Δ) + N2	O2 + N2	1.5D-24
113	O3 +M	O+O2 +M	3.92D-16*exp(-11.4D3/Tg)
114	NO + NO2 +M	N2O3 +M	3.09D-46*(300/Tg)**7.7
115	NO+ H +M	HNO + M	1.0D-44*exp(3.0D2/Tg)
116	NO + HO2	OH + NO2	3.4D-18*exp(270/Tg)
117	NO2 + NO2 +M	N2O4 +M	1.17D-45*(3.0D2/Tg)**3.8
118	NO2 + H	OH + NO	1.47D-16
119	NO2 + OH+ M	HNO3 +M	2.2D-42 (3.0D2/Tg)**2.9
120	NO3 + NO3	NO2 + NO2 + O2	5.0D-18*exp(-3.0D3/Tg)
121	NO3 + HO2	NO2 + OH+O2	4.8D-18
122	NO3 + HO2	HNO3 + O2	9.2D-19
123	N2O3 +M	NO+NO2 +M	1.03D-16*exp(-2.628D3/Tg)
124	N2O4 +M	NO2 + NO2 +M	1.09D-13*exp(-4.952D3/Tg)
125	OH + OH +M	H2O2 +M	6.9D-43*(Tg/3.0D2)**-0.8
126	OH + HNO2	NO2 + H2O	1.8D-17*exp(-3.9D2/Tg)
127	HNO + O2	NO+HO2	5.25D-18*exp(-1.51D3/Tg)
128	HNO + O2	NO2 + OH	1.66D-21
129	HNO + HNO	N2O+H2O	1.4D-21*exp(-1.6D3/Tg)
130	HNO2 + HNO2	NO+NO2 + H2O	1.0D-26
131	HNO2 + HNO3	NO2 + NO2 + H2O	1.6D-23

Reaction No	COMMENTS
1	Kossyi, Kostinsky, Matveyev, Silakov 1992 pg.210 Equation 44 :- K=6E-39*(300/Te)**1.5
2	Kossyi, Kostinsky, Matveyev, Silakov 1992 pg.209 Equation 38 :- K=2.8E-13*(300/Te)**0.5

3	Kossyi, Kostinsky, Matveyev, Silakov 1992 pg.209 Equation 39 :- $K=2.0E-13*(300/Te)**0.5$
4	Kossyi, Kostinsky, Matveyev, Silakov 1992 pg.210 Equation 44 :- $K=6E-39*(300/Te)**1.5$
5	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.141 Table 8.11 Equation 4:- $K=2E-13*(300/Te)**0.5$
6	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.141 Table 8.11 Equation 5 :- $K=2E-12*(300/Te)**0.5$
7	Kossyi, Kostinsky, Matveyev, Silakov 1992 pg.210 Equation 44 :- $K=6E-39*(300/Te)**1.5$
8	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.141 Table 8.11 Equation 2:- $K=1.6E-13*(300/Te)**0.55$
9	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.141 Table 8.11 Equation 2:- $K=2.7E-13*(300/Te)**0.7$
10	Kossyi, Kostinsky, Matveyev, Silakov 1992 pg.210 Equation 44 :- $K=6E-39*(300/Te)**1.5$
11	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.141 Table 8.11 Equation 8:- $K=1.4E-13*(300/Te)**0.5$
12	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.141 Table 8.11 Equation 6 :- $K=2E-13*(300/Te)**0.5$
13	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.141 Table 8.11 Equation 3 :- $K=4.2E-13*(300/Te)**0.85$
14	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.141 Table 8.11 Equation 3 :- $K=4.2E-13*(300/Te)**0.85$
16	Kossyi, Kostinsky, Matveyev, Silakov pg.210 Equation 44 :- $K=6E-39*(300/Te)**1.5$
17	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.141 Table 8.11 Equation 7 :- $K=2E-13*(300/Te)**0.5$
18	Williams,Adams,Babcock,Herd ,Geoghegan M 1996 there is a no equations
19	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.141 Equation13 Table 8.11 :- $K=1.55E-13*(300/Te)**0.97$
20	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.141 Equation13 Table 8.11 :- $K=1.55E-13*(300/Te)**0.97$
21	Williams,Adams,Babcock,Herd ,Geoghegan M 1996 there is a no equations
22	Williams,Adams,Babcock,Herd ,Geoghegan M 1996 there is a no equations
23	Williams,Adams,Babcock,Herd ,Geoghegan M 1996 there is a no equations
24	Williams,Adams,Babcock,Herd ,Geoghegan M 1996 there is a no equations
25	Chanin, Phelps, Biondi 1962 pg.229 There is no equations
26	Chanin, Phelps, Biondi 1962 pg.229 There is no equations
27	Olson, Peterson, Moseley 1970 pg 3394 Table II There is no equation
28	Cenian, Chernukho, Borodin 1995 pg.289 Appendix Collisional detachment E11 $K=2.3E-11$
29	Mcfarland,Dunkin, Fehsenfeld,Schmeltekopf,Ferguson pg2359 Table II 7th equation: $K=3.28E-19$
30	Mcfarland,Dunkin, Fehsenfeld,Schmeltekopf,Ferguson pg2359 Table II 7th equation: $K=3.28E-19$
31	Mcfarland,Dunkin, Fehsenfeld,Schmeltekopf,Ferguson pg2359 Table II 3rd

	equation: $K=4.26E-10$
32	Mcfarland,Dunkin, Fehsenfeld,Schmeltekopf,Ferguson pg2359 Table II 1st equation: $K=2.32E-10$
33	Olson, Peterson, Moseley 1970 pg 3394 Table II:-There is no equation
34	Olson, Peterson, Moseley 1970 pg 3394 Table II:-There is no equation
35	Anicich 1993 pg1503 Table of reactions 16th equation:- $K=5.5E-16$
36	Anicich 1993 pg1503 Table of reactions 16th equation:- $K=5.5E-16$
37	Sieck, Herron, Green 2000 pg. 240 Table 1 R3: $K=3.3E-16$
38	Stalder, Vidmar,Nersisyan, Graham 2006 pg3. Table 1:There is no equation
39	Stalder, Vidmar,Nersisyan, Graham 2006 pg3. Table 1:There is no equation
40	Stalder, Vidmar,Nersisyan, Graham 2006 pg3. Table 1:There is no equation
41	Stalder, Vidmar,Nersisyan, Graham 2006 pg3. Table 1:There is no equation
42	Sieck ,Herron, Green 2000 pg.240 Table 1: There is no equation
43	Dorai, Kushner 2003 pg.670 Equation 21: $K=5.1E-11$
44	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.183 Table 10.7 R40 :- $K=2.1E-23*(T_{gas}/121)$
45	Dorai, Kushner 2003 pg.671 Equation 23: $K=2.5E-16$
46	Dorai, Kushner 2003 pg.671 Equation 23: $K=2.5E-16$
47	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.181 Table 10.8 R57:- $K=3.0E-16*\exp(-1800/T_{gas})$
48	Kossyi, Kostinsky, Matveyev, Silakov 1992 pg.215 Equation 191 $K=3.0 E-18$
49	Stalder, Vidmar,Nersisyan, Graham 2006 pg3. Table 1:There is no equation
50	Stalder, Vidmar,Nersisyan, Graham 2006 pg3. Table 1:There is no equation
51	Bohringer, Arnold, Smith , Adams 1983 pg.25: $K=5.5E-31*(300/T_{gas})^{**2.7}$
52	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.182 Table 10.9 R3 :- $K=1.2E-15$
53	Matzing H 2007 pg.370 Table III R228:- $K=3.0E-16$
54	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.183 Table 10.9 No equation
55	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.182 Table 10.9 R14:- $K=2.6E-18$
56	Anicich 1993 pg1554 Table of reactions 22nd equation $K=2.3E-16$
57	Anicich 1993 pg1554 Table of reactions 22nd equation $K=2.3E-16$
58	Anicich 1993 pg1554 Table of reactions 22nd equation $K=2.3E-16$
59	Anicich 1993 pg1554 Table of reactions 18th equation:- $K=2.7E-16$
60	Anicich 1993 pg1554 Table of reactions No equation
61	Dorai, Kushner 2003 pg.671 Equation 27: $K=5.1E-27$
62	Dorai, Kushner 2003 pg.670 Equation 20: $K=1.1E-29$
63	Anicich 1993 pg1474 Table of reactions 6th equation:- $K=7.30E-15$
64	Anicich 1993 pg1474 Table of reactions 6th equation:- $K=7.30E-9$
65	Anicich 1993 pg1474 Table of reactions 6th equation:- $K=7.30E-9$
66	Anicich 1993 pg1511 Table of reactions 16th equation:- $K=1.33E-15$
67	Sieck ,Herron, Green 2000 pg.240 Table I There is no equation
68	Sieck ,Herron, Green 2000 pg.240 Table I R12: $K=2.8E-15$
69	Olson, Peterson, Moseley 1970 pg.3394 Table II There is no equation
70	Kossyi, Kostinsky, Matveyev, Silakov 1992 pg.217 Equation 266 $K=1.0 E-$

	16
71	Matzing H 2007 pg.375 Table IV R318:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
72	Matzing H 2007 pg.373 Table IV R288:-K=(2.6E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
73	Matzing H 2007 pg.373 Table IV R289:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
74	Matzing H 2007 pg.374 Table IV R290:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
75	Matzing H 2007 pg.373 Table IV R281:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
76	Matzing H 2007 pg.373 Table IV R282:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
77	Matzing H 2007 pg.373 Table IV R278:-K=(1.6E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
78	Matzing H 2007 pg.373 Table IV R280:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
7980	Matzing H 2007 pg.387 Table IV R506:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
81	Matzing H 2007 pg.387 Table IV R504:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
82	Matzing H 2007 pg.387 Table IV R505:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
83	Matzing H 2007 pg.387 Table IV R506:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
84	Matzing H 2007 pg.386 Table IV R503:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
85	Matzing H 2007 pg.386 Table IV R502 :-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
86	Matzing H 2007 pg.387 Table IV R508:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
87	Matzing H 2007 pg.375 Table IV R308:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
88	Matzing H 2007 pg.384 Table IV R454:-K=(3.5E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
89	Matzing H 2007 pg.383 Table IV R449:-K=(4.9E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
90	Matzing H 2007 pg.384 Table IV R458:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
91	Matzing H 2007 pg.386 Table IV R500:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
92	Matzing H 2007 pg.386 Table IV R493:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
93	Matzing H 2007 pg.386 Table IV R494:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
94	Matzing H 2007 pg.386 Table IV R495:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)
95	Matzing H 2007 pg.386 Table IV R501:-K=(4.0E-13*(300/Tgas)**0.5)+((3.0E-25*(300/Tgas)**2.5)*M)

96	Matzing H 2007 pg.386 Table IV R491:- $K=(4.0E-13*(300/T_{gas})^{**0.5}+((3.0E-25*(300/T_{gas})^{**2.5})*M)$
97	Matzing H 2007 pg.386 Table IV R492:- $K=(4.0E-13*(300/T_{gas})^{**0.5}+((3.0E-25*(300/T_{gas})^{**2.5})*M)$
98	Matzing H 2007 pg.386 Table IV R497:- $K=(4.0E-13*(300/T_{gas})^{**0.5}+((3.0E-25*(300/T_{gas})^{**2.5})*M)$
99	Kossyi, Kostinsky, Matveyev, Silakov 1992 pg.213 Equation 137:- $K=6.0E-11$
100	Matzing H 2007 pg.389 Table II No equation
101	Matzing H 2007 pg.389 Table II No equation
102	Matzing H 2007 pg.389 Table II No equation
103	Matzing H 2007 pg.389 Table II No equation
104	Matzing H 2007 pg.389 Table II No equation
105	Herron, Green 2001 pg.469 Table II Ox reaction 3rd equation: $K=6.0E-46*\exp(T_{gas}/300)^{**-2.8}$
106	Dorai, Kushner 2003 pg.671 Equation 26: $K=1.7E-9$
107	Matzing H 2007 pg.394 Table VI R716 $K=1.66E-19$
108	Dorai, Kushner 2003 pg.671 Equation 40: $K=2.3E-11*\exp(110/T_{gas})$
109	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.161 Table 9.6 :- $K=6.4E-12*\exp(-67/T_{gas})$
110	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.161 Table 9.6 :- $K=8.0E-12$
111	National Institute of Standards and Technology, cited 2011:NIST Chemical Kinetics Database :- $K=1.0E-11$
112	National Institute of Standards and Technology, cited 2011:NIST Chemical Kinetics Database :- $K=4.0E-11$
113	Atkinson, Baulch, Cox , Hampson, Kerr, Rossi,Troe 1999 pg.1332 Table 2 Ox reaction R1347: $K=1.4E-25$
114	Jeong, Park, Henins, Babayan, Tu, Selwyn,Ding, Hicks R F 2000 pg.8030 Table 1 R4: $K=7.26E-10*\exp(-11400/T_{gas})$
115	National Institute of Standards and Technology, cited 2011:NIST Chemical Kinetics Database :- $K=3.09E-43*(300/T_{gas})^{**7.7}$
116	Person, Ham 1988 pg.7 Appendix I: $K=3.4E-44$ 8th equation
117	Dorai, Kushner 2003 pg.671 Equation 35: $K=3.8E-11*\exp(85/T_{gas})$
118	National Institute of Standards and Technology, cited 2011:NIST Chemical Kinetics Database :- $K=1.49E-45$
119	Capitelli, Ferreira, Gordiets, Osipov 2000 pg.173 Table 10.4 R27:- $K=1.7D-17*\exp(1000/T_{gas})$
120	Herron, Green 2001 pg.468 Table II Nox reaction Equation 4: $K=2.6E-42*\exp(T_{gas}/300)^{**-2.9}$
121	Kossyi, Kostinsky, Matveyev, Silakov 1992 pg.213 Equation 88:- $K=1.5D-12*(3000/T_{gas})$
122	Stalder, Vidmar,Nersisyan, Graham 2006 pg3. Table 1:There is no equation
123	Dorai, Kushner 2003 pg.672 Equation 52: $K=9.7E-12$
124	National Institute of Standards and Technology, cited 2011:NIST Chemical Kinetics Database :- $K=2.01E-13*\exp(-2628/T_{gas})$
125	National Institute of Standards and Technology, cited 2011:NIST Chemical Kinetics Database :- $K=1.33E-11*\exp(-4952/T_{gas})$
126	Dorai, Kushner 2003 pg.671 Equation 50: $K=6.9E-31*(T_{gas}/298)^{**-0.8}$

127	Dorai, Kushner 2003 pg.671 Equation 56: $K=1.8E-11*(390/T_{gas})$
128	Dorai, Kushner 2003 pg.671 Equation 17: $K=5.2E-11*(-2840/T_{gas})$
129	Matzing H 2007 pg.391 Table VI R174 $K=1.6 E-19$
130	Matzing H 2007 pg.391 Table VI R717 $K=6.56 E-19*exp(-2900/T_{gas})$
131	Matzing H 2007 pg.391 Table VI 6th equation $K=1.0 E-9$
132	Matzing H 2007 pg.397 Table VI 8th equation $K=5.0E-9$

The references for rate coefficients are distinct from the actual material, as noted in the comments. In the preceding model from Sakiyamai, only non-satisfied rate coefficients are discussed. Out of 624 rate coefficients, was discovered 132 that do not satisfy the references.

13. RESULTS OBTAINED:

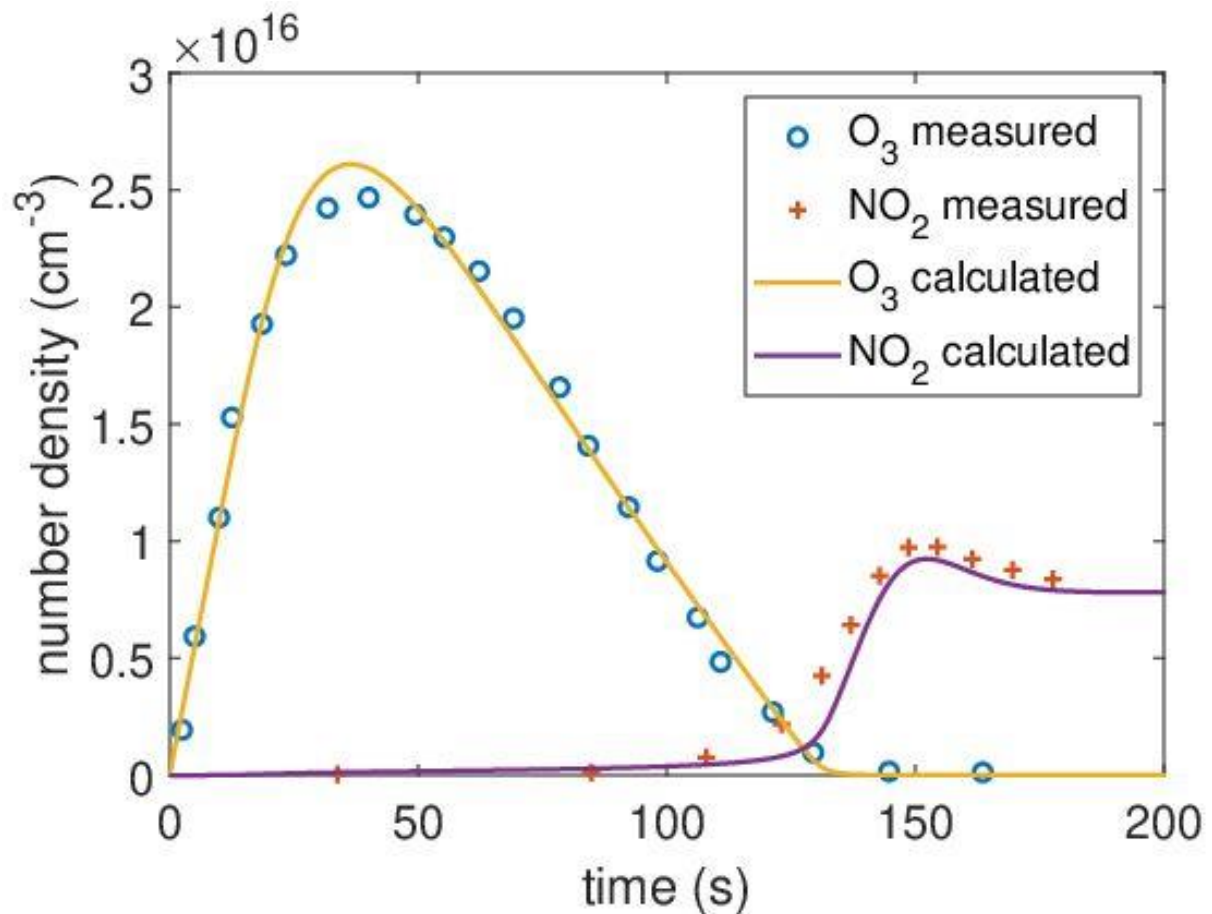


Figure 19

COMMENTS:

The kinetic models described in this thesis are of great importance because they can be used to understand the chemical phenomena induced by electrical discharges in air. Figure 19. represents the trend over time of ozone and nitrogen dioxide produced by a Superficial Barrier Discharge (SDBD). Experimental data obtained by the research group in the Physics Department of the University Milano Bicocca are compared with the numerical results. The study highlighted how the initial ozone formation is inhibited and cancelled by nitrogen oxidation processes.

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