# CHEMICAL REACTIONS IN ELECTRICAL PLASMAS[1, 2]

GENE G. MANNELLA

*NASA Electronics Research Center, Cambridge, Massachusetts*

## ABSTRACT

Some fundamental characteristics of chemical species in plasmas are reviewed to indicate the necessity for more complete description of the energy states involved. Bsaic modes of energy storage and their connection with the thermodynamics and chemical kinetics of these species are discussed.

## INTRODUCTION

The original Greek word "plasma" means mold or matrix. It was, as applied by scientists in Germany, used to describe that portion of the conduction column in an arc discharge between the anode and cathode fall regions. This classical definition, therefore, would limit plasma to an electrically pseudo-neutral, viscous, electrically conducting, fluid mass of appreciably ionized gas or vapor. Modern usage includes gases produced by shock waves or other devices that do not involve a flow of electricity, and ionized gases that are present in a glow discharge.

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Chemists have always been interested in the interaction of electricity and matter. Historically, however, the lack of adequate measuring techniques and suitable theory has forced the chemists to focus their attention not on the plasma, but on the products issuing from the discharge. More recently, a resurgence of interest in the energy transfer mechanisms within the discharge itself has made diagnostics of the plasma an area of prime interest (Mannella, 1961).

## BACKGROUND

Today a plasma is defined as a gaseous mixture of ions and electrons with or without the presence of neutral particles and with or without the presence of an applied electric field. To characterize the plasma, electrical conductivity, regardless of whether an actual applied potential is present, is a convenient parameter and is frequently used. However, conductivity is manifest only because of ionization, so that it is also logical to make the definition more fundamental by emphasizing the ionization phenomena.

Confusion generally arises because materials have vastly different ionization potentials. For instance, some metals such as cesium or potassium have sufficiently low primary ionization potentials to be highly ionized at 3000 to 3500°K. However, above temperatures of 10,000°K, any plasma has an electrical conductivity *roughly equivalent to that of a metallic conductor. One very significant difference,* however, is that the plasma is also a compressible fluid, so that its behavior in an electric or magnetic field is strongly influenced by the laws of fluid mechanics, in addition to those governing electromagnetic phenomena. This particular feature forms the basis for the rather new science of magnetohydrodynamics or MHD (MAB, 1960).

The area assigned to plasma chemistry can best be identified by examining the question of what happens to a gas as the temperature is increased. This behavior can be fairly well predicted and is shown below using nitrogen as an illustrative example.

Effect of Increasing Temperature on the Composition
of Nitrogen Gas

| *Temperature, °K* | *Effect* |
|---|---|
| 2,000 | No change except an increase in kinetic energy. |
| 7,000 | Gas is 33 percent dissociated, 1 percent ionized.<br>Some electronic excitation of atoms and molecules. |
| 12,000 | Gas is 100 percent dissociated, 14 percent ionized.<br>It is now a good electrical conductor. |
| 20,000 | Double ionization begins. |
| 30,000 | Gas is 100 percent ionized with $[N^+] = [N^{++}]$. |

At temperatures above 15,000°K, few chemical bonds exist, the gas being highly ionized and rapidly approaching the realm of plasma physics. The interval from 5,000 to 15,000°K is one in which the chemical nature is severely altered, but where bonds still exist, although the particles present are considerably different than those normally encountered in more classical high-temperature processes, such as combustion. In such a low-temperature, or chemical plasma, the species which can be present are listed below:

Representative Species Present in a Nitrogen Plasma

| *State* | *Atomic Species* | *Molecular Species* |
|---|---|---|
| Ground | $N(^4S)$ | $N_2(X^1\Sigma_g^+)$ |
| Electronically excited | $N(^2P)$ | $N_2(B^3\Pi g)$ |
| Ionized-positive | $N^+$ | $N_2^+$ |
| Ionized-negative | $N^-$ | $N_2^-$ |
| Ionized-excited | $(N^+, N^-)^*$ | $(N_2^+, N_2^-)^*$ |

Some of these species are very much less likely to exist than others. Most of the atoms will probably be in their ground state since electronic excitations correspond to energies equivalent to very high temperatures. Positive ions, of course, should be plentiful. Formation of negative ions is not too likely, even in very electronegative gases. (Negative ion formation is not favored by extremely high temperatures and may occur only in the periphery of the plasma flame.)

An identification for various types of plasmas can be made on an arbitrary basis as follows:

| *Type* | *Identifying Characteristic* |
|---|---|
| Low–temperature or chemical plasma | 5,000 to 15,000 °K |
| Low-density | 10 mm or lower |
| High-density | 10 mm or higher |

The last two characteristics may appear somewhat superfluous, but are of value in consideration of the temperature of the plasma. At low densities, the temperature of the electrons is very much higher than the temperature of the ions or of the neutral particles. This can readily be understood by noting that, in electrical plasmas, energy is transferred to the gas by the action of the applied electrical field, which accelerates the charged particles. This increases their kinetic energy, which is then transferred to the bulk of the gas by collisions which raise the overall temperature. Because of their greater mobility, the free electrons have a higher kinetic energy, or temperature (since the definition of one of these variables is made in terms of the other), than the other particles (Stratton, 1961). As the pressure is increased, the number of collisions increases. Beyond a certain pressure, all three types of particles have more or less the same temperature; this would be the beginning of the high-pressure discharge. In this latter type of discharge, a thermal plasma generally exists, where local thermodynamic equilibrium prevails and all neutral and charged particles are at the same temperature (Giannini).

Although temperature is based on random thermal motion, and a plasma has some directed motion, Langmuir very early made a connection between the two. It is interesting to note that, by his analysis, one electron volt of excitation is equivalent to 11,000°K. The total energy of a plasma, then, can consist of the following:

1. Directed kinetic energy (directed movement of plasma as a whole).
2. Random thermal energy (vibrational, rotational and electronic excitation and undirected translational energy).
3. Dissociation energy.
4. Ionization energy.

## DISCUSSION

In general, plasma chemistry differs from ordinary chemistry in that no solids are present at temperatures above 5,000°K and at pressures of 1 atmosphere or less, because ions and electrons are common species and because the particles have a greater kinetic energy, on the average, than in other states. Most molecules are dissociated into atoms even below 5000°K and, as temperatures increase beyond this, more and more chemical bonds are broken. Further, plasma chemistry involves new environments and introduces new variables that are not very well understood. Whereas ordinary chemical experience suggests that simple substances become increasingly active with temperature and form compounds, there obviously comes a temperature at which this trend reverses and the chemical bonds are broken. Many of the compounds which are formed under these conditions are likely to be metastable, but may persist at ordinary temperatures if quenched rapidly enough. Interactions between ions and molecules (possibly in excited states) may stabilize unusual species in plasmas, species which can serve as reaction intermediates for unexpected chemical products.

With regard to diagnostics and characterization of plasma gases, the determination of species present and other observations and measurements required for the proper characterization of a given plasma makes demands upon both plasma physics and plasma chemistry. A basic problem concerns the measurement of temperature and temperature profiles in plasmas. It is interesting to point out that a satisfactory definition and standard for temperature above 5,000°K does not exist. Optical spectroscopy for the atoms, ions, and molecules present is the principal tool used for the study of species in a plasma. Other analytical tools, such as X-ray density measurements, microwave reflection and adsorption, and specially designed mass spectrometer probes, are also to be considered (Biondi, 1955). One of the most reliable methods of temperature measurement in a plasma is the use of a spectrograph to measure the width of various atomic lines radiated from the plasma (Nilsson, 1959). This technique requires a spectrograph of very good dispersion and reliability, and is not particularly easy or rapid. (Duffenback and LaRue, 1941.)

Among the important kinetic problems involved in plasma chemistry the following must be included:

1. The nature of ion-molecule reactions and charge transfer processes.
2. The nature of atom-condensed phase and ion-condensed phase interactions.
3. The role of excited electronic states in chemical kinetics.
4. Chain reactions in high-temperature systems.
5. Transport properties of plasmas.

The simplest way to study a complex kinetic system is to resolve it into elementary reactions and to study each reaction separately. Most elementary reactions are strongly dependent on temperature, but the present theory of reaction rates is in such a state that extrapolation over a factor of two in absolute temperature becomes hazardous. We cannot, therefore, rely upon our knowledge of chemical kinetics to supply any *a priori* information about reactions in a plasma. One would, however, expect the reactions of neutral molecules (such as decomposition, recombination, and metathesis) to follow the same laws which have been worked out for ordinary temperatures and pressures. There is the possibility, however, that a complete change of mechanism may occur, thus invalidating the applicability of low-temperature data.

In addition, at 5,000°K, charged species will be present and reactions involving charged species are expected to involve quite unusual reaction cross-sections (which already have been observed in ion-molecule reactions in a mass spectrometer). Unusual reactions which must be expected would be those involving thermal ionization, ionic recombination, ion-molecule reactions, and recombination by electron addition to a positive molecular ion which results in radiation. The use of molecular beams, shock tubes, mass spectrometers, and other well-designed special methods is indicated for a fundamental study of these new types of reactions. The additional burden of designing new equipment and techniques to study these very difficult kinetic systems must also be recognized.

Chemical kinetics not only includes the interaction of molecules with each other, but also the interaction of molecules with surfaces. When a plasma jet hits a cold surface, the elementary processes that occur are those which have been or can be studied by impinging a molecular beam on a surface. These elementary processes include reflection, sticking, charge transfer, atom abstraction from the solid, penetration with sputtering, etc. With present beam techniques, 5,000°K is inconveniently high for thermal beams and inconveniently low for charge particle beams. Thus, there is room for straightforward extension of existing techniques into the region of plasma chemistry.

From the standpoint of the considerable amounts of energy storable in a plasma, chemical studies will obviously be oriented towards elucidating the nature of the reactions involved in the transfer of energy within the plasma regime. However, this will not be a straightforward extension of flame chemistry because of the vastly different species involved.

The existence of species of the type mentioned above forces an extension of chemical kinetics principles. The following reaction serves as an illustration:

$$H_2 + 1/2O_2 \rightarrow H_2O(g) \qquad \Delta H_{25^\circ C} = -57.8 \text{ kcal/mole}$$

This type of reaction serves to indicate the relative quantities of reactants involved. Questions of mechanism, steric considerations, etc., are left unanswered. For this reason, this type of reaction may be termed a stoichoimetric statement and is really the simplest form of representing a chemical reaction.

In considering the reaction of more basic particles, i.e. atoms instead of molecules, the following types of reactions are more informative:

$$O + O + M \rightarrow O_2 + M \qquad -119 \text{ kcal/mole}$$
$$O + O_2 + M \rightarrow O_3 + M \qquad -26 \text{ kcal/mole}$$

This reaction statement is more descriptive, giving information regarding the chemical state of the reactant and the mechanism involved in gas-phase formation of ozone. This type of reaction statement may then be termed chemicokinetic because it combines the aspects of chemical state and reaction kinetics.

However, a further step is required in describing the type of reactions possible in plasma regimes, since energy may be stored by the species in modes other than dissociation. A reaction of the type

$$N(^4S) + NO(X\Pi^2) \rightarrow N_2(X^1\Sigma) + O(^3P) \qquad \Delta H = -75 \text{ kcal/mole}$$

now must be used to describe the electronic state of the reactants. A further refinement beyond this would involve assignment of the vibrational and rotational quanta associated with the molecular species. A reaction of this type, informative of both mechanism and complete energy state of the reactants, may be termed physicokinetic.

Since kinetics of excited species play a major role in the reactions in plasma flames, it is well to note several seldom-encountered rules which govern the reactions of such species. First, the spin of the reactants must be conserved, i.e.:

$$\bar{S} = (S_1 + S_2),\ (S_1 + S_2 - 1) \ldots (S_1 - S_2)$$

This states that the vector sum of the spins of the products must bear an integral relationship to the vector sum of the spins of the reactants (Laidler, 1950). Spin-disallowed reactions are not common, but must be considered as an everpresent possibility.

The second rule is that a resonance condition is favored in collisions of the second kind, which is important since collisions of excited species may involve transfer of potential energy. This rule "quantizes" the reaction. An example of such a resonance collision is the following:

$$N_x(A^3\Sigma_u^+) + NH(X^3\Sigma^-) \rightarrow N_2(X^1\Sigma) + NH(C^1\Pi) \qquad \Delta H \approx 0$$

When investigating energy transfer mechanisms in plasmas, this type of resonance condition serves as a restraining condition. The extent of deviation from resonance is inversely proportional to the probability of the reaction (Herzberg, 1944).

## CONCLUSIONS

The advent of plasma chemistry is coupled with a serious need for the further development of our knowledge of chemical kinetics. The trend toward higher temperatures and higher energy systems, particularly in aerospace applications, will result in excited species being encountered more frequently. The need for understanding the interactions of these particles is hence obvious. When coupled with the strong academic appeal of these heretofore rare species, this need should undoubtedly result in substantial progress in our knowledge of the fundamental behavior of light atoms and molecules.

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