REACTIONS UNDER PLASMA CONDITIONS

Volume II

Edited by M. VENUGOPALAN

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M. VENUGOPALAN
Western Illinois University

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Contributors to Volume II

H. F. CALCOTE, AeroChem Research Laboratories, Inc., O. P. Box 12, Princeton, New Jersey.

W. C. GARDINER, JR., The University of Texas at Austin, Department of Chemistry, Austin, Texas.

G. V. KARACHEVTSEV, Institut Khimicheskoi Fiziki, Akademiya Nauk SSSR, Vorobjevskoje Shausse 2B, Moskwa V-334, U.S.S.R.

G. LEHNER, Institut für Plasmaphysik, 8046 Garching bei München, Germany.

W. J. MILLER, AeroChem Research Laboratories, Inc., P. O. Box 12, Princeton, New Jersey.

L. POLAK, Institut Neftekhimicheskogo Sinteza, Akademiya Nauk SSSR, Lenin Prospect 29, B-71, Moskwa, U.S.S.R.

M. M. SHAHIN, Research and Engineering Sciences Division, Xerox Corporation, Rochester, New York.

C. S. STOKES, Research Institute of Temple University, 4150 Henry Avenue, Philadelphia, Pennsylvania.

V. L. TAL'ROSE, Institut Khimicheskoi Fiziki, Akademiya Nauk SSSR, Vorobjevskoje Shausse 2B, Moskwa V-334, U.S.S.R.

M. VENUGOPALAN, Western Illinois University, Department of Chemistry, Macomb, Illinois.

F. VURSEL, Institut Neftekhimicheskogo Sinteza, Akademiya Nauk SSSR, Lenin Prospect 29, B-71, Moskwa, U.S.S.R.

Editor's Note

In the framework of cosmology, the engineering and technological utility of the plasma or ionized state of matter began with the origin of the universe. For mankind, however, it has been a comparatively recent field of study. Thanks largely to the pioneering experiments of many twentieth-century scientists, many aspects of the exotic nature of the plasma state have at long last been revealed. The study of plasmas has since developed with such amazing rapidity that there already exist several books on plasma physics. However, the interest in plasma chemistry and plasma chemical technology has developed only much more recently and only a beginning has been made in the production of chemicals using plasmas. This is evidenced by the limited number of publications that have appeared until recently in this field and by the very few books that have been published.

However, there has never been an attempt to correlate in any single book or under one title the bulk of information currently available on both the physics and chemistry of plasmas, together with the necessary theoretical and experimental background. The need for such a book is justified as the barriers between physics and chemistry are being narrowed each day, and as we face groups of scientists interested in both the chemistry and physics of the plasma state. The fundamental physical theories and properties of the plasma state, the types of reactions that can be achieved in such a medium, and the practical methods that can be applied for their investigation are of great interest to them. It is for these plasma scientists and their students that the present book on reactions under plasma conditions is designed.

This book is intended to give a survey of the reactions under plasma conditions and is presented in two volumes.

Volume 1 includes a general discussion of the plasma state of matter and the fundamental definitions and relationships pertinent to it (Chapters 1 and 2); thermodynamic properties of the equilibrium and nonequilibrium states of plasmas (Chapter 3), and transport properties of plasmas (Chapter 4);

experimental methods of plasma production, together with the necessary theoretical background (Chapters 5 and 6); and theories and practices of the various techniques useful in plasma analysis, such as spectroscopic (Chapter 7), microwave, and laser techniques (Chapter 8), the electric probe methods (Chapter 9), and ion mass-spectrometry (Chapter 10).

Volume 2 begins with an introduction to plasma chemistry (Chapter 11) and includes detailed discussions of the elementary reactions (Chapter 12) and of the principles of nonequilibrium reaction kinetics (Chapter 13) in plasmas; surveys of chemical reactions investigated in electrical discharges (Chapter 14), in plasma jets (Chapter 15), and a discussion of plasma chemical processing (Chapter 16); reviews of the recent investigations of reactions in flame plasmas (Chapter 17), in shock-wave generated plasmas (Chapter 18), and in plasmas obtained by irradiation with electromagnetic rediations and by bombardment with high-energy particles (Chapter 19); and finally, a discussion of the nuclear reactions in fully ionized plasmas at high temperatures (Chapter 20).

In both volumes, wherever it was found necessary, adequate descriptions of work on natural plasmas have been included, although the main emphasis has been on the studies of laboratory plasmas.

In view of the wide range of topics covered in a multi-author survey such as this book, some overlapping of the subject matter was inevitable. Although I have made every effort to minimize such overlapping of material from chapter to chapter, this could be considered an advantage in many chapters, since it even serves to widen the basis of understanding.

The book was planned in the fall of 1967, when I was on the staff of the Royal Military College of Canada, Kingston, Ontario. In fact, work on the book began early in 1968 and many of the chapters were prepared as recently as March 1969. Except for some minor additions and later revisions, these chapters were finalized in July 1969. Unfortunatley, the preparation of the remaining chapters and thus the completion of the book took a much longer time than anticipated. Therefore, some of the very latest developments may be missing from certain chapters. Nevertheless, it is hoped that the book will serve as a source of coordinated information for plasma scientists of the present and the future as well.

I am very fortunate in having scientists from many countries agree to cooperate in the preparation of the text and contribute substantially to the book. I wish to thank these contributors and, particularly those authors whose advice has been most helpful in the organization of the book. Indeed, the book in its present form owes much to the many suggestions, which I solicited and readily received, from several scientists, especially some of its contributors, Dr. H. W. Drawin, Professor L. Polak, and Dr. M. M. Shahin. To them and to those contributors who prepared their chapters within a short period, I am very much indebted.

M. VENUGOPALAN

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Reactions Under Plasma Conditions

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CHAPTER ELEVEN

Plasma Chemistry—An Introduction

M. VENUGOPALAN

I. INTRODUCTION

Although the nineteenth century was relatively active in plasma chemistry, using electric arcs for high-temperature solid state reactions (1), material preparation (2), and gaseous syntheses of endothermic molecules (3), it is

only recently that numerous laboratories have directed a concerted effort to understanding the advantages of plasmas for chemical and nuclear reactions. This impetus was due to the realization that the early work was largely empirical in nature and was accomplished with little knowledge of the nature and temperatures of plasmas. The types of species produced and their relative abundance in plasmas are no doubt determined by the conditions that exist within the plasma. On the other hand, the increased scientific understanding of the nature of plasmas built up during this century and the development of new techniques for plasma experimentation following World War II have made advanced chemical and nuclear research with plasmas possible in a controlled fashion. The recent interest in plasma chemistry stems from the possibility of producing adequate quantities of known species in plasmas and their usefulness in studying reaction kinetics and molecular and nuclear syntheses.

The chief purpose of this introductory chapter is to call attention to the unique possibilities for studying the reactions of species which are available in plasmas and to the problems which must be resolved in plasma chemistry. Whereas a considerable amount of work in plasma chemistry involves the use of the so-called low-temperature $(T < 10^5 \, ^\circ\text{K})$plasma for molecular or chemical synthesis, high-temperature $(T > 10^7 \, ^\circ\text{K})$ plasma is interesting in its own right. The latter finds application in achieving nuclear synthesis, that is, the synthesis of heavier nuclei from lighter ones. We shall therefore also be concerned in this chapter with this aspect of plasma chemistry.

II. DEFINITIONS AND PRINCIPLES

Plasma chemistry is concerned with reactions occurring in plasmas, whose properties have already been discussed in the first few chapters of this book. The title also includes reactions between plasma particles and those comprising the material constituting the containing walls of the reactor and electrodes, if any. Since ions and electrons are common species and even neutral particles have great kinetic energy in a plasma, plasma chemistry is quite different from ordinary chemistry. Atoms in highly excited states may react to give compounds which are unlikely to be formed in conventional chemical reactions.

Since plasma temperatures often lie just above those at which chemical bonds can exist, the term " plasma chemistry " may in a sense be a misnomer. This situation has led to a variety of definitions (4) such as " chemistry that utilizes the high temperature and high energies produced in plasmas in reactions at lower temperatures, or where the high rates of heat transfer available

from plasmas are used to effect a chemical or physical change," "the application of the temperatures and energies which can be achieved in plasmas to chemical problems" and "the reactions which can occur best at the very high temperatures which can be most conveniently generated using thermal plasmas." Unfortunately, some of these definitions do not include under the title "plasma chemistry" a large number of chemical reactions occurring in low-pressure glow discharges in which the atoms, though active, are near room temperature, nor do they include nuclear reactions that may be achieved in high-temperature plasmas.

It has been the practice for some time to classify plasmas into three main categories: plasmas in complete thermodynamic equilibrium (CTE plasmas), plasmas in local thermodynamic equilibrium (LTE plasmas), and plasmas in nonlocal thermodynamic equilibrium (non-LTE plasmas). Most laboratory plasmas, except those used for thermonuclear fusion experiments, belong to the two latter categories. Figure 1 shows typical plasmas characterized by their densities and energies. It does not, however, show transient plasmas generated by shock waves, exploding wires, and electrical resistance heating techniques at very high pressures, nor does it indicate the regions of plasmas maintained by nuclear fragmentation. Plasmas generated by electron and photon beams, which are indicated in Fig. 1, belong to the non-LTE category.
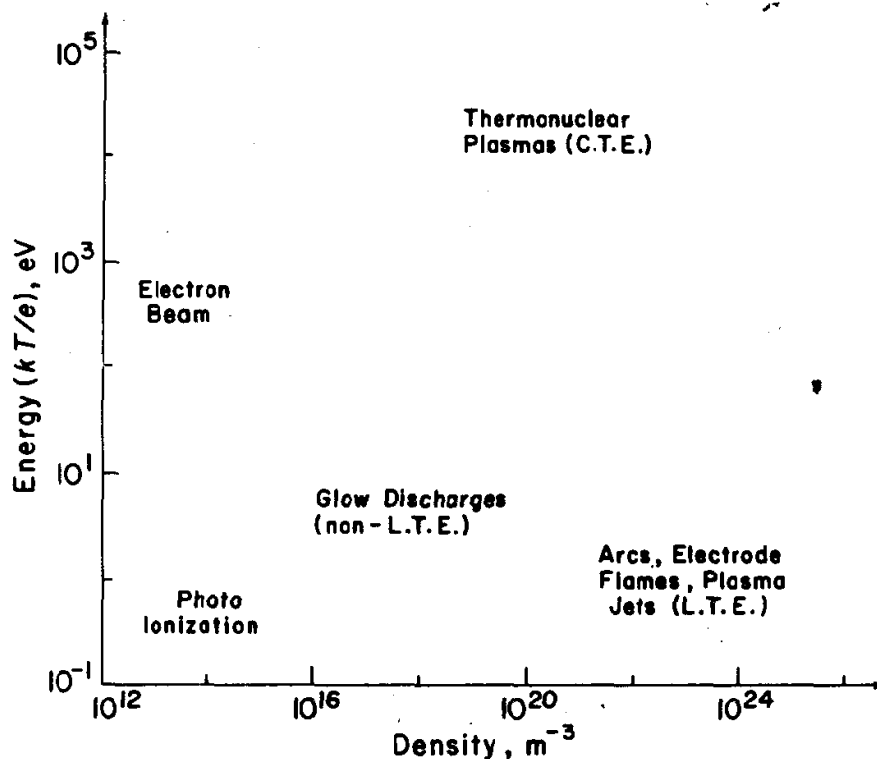

Figure 1 Typical plasmas characterized by their energies and densities.

In chemical literature it is not unusual to find LTE plasmas referred to as thermal or " hot" plasmas and non-LTE plasmas referred to as nonthermal or "cold" plasmas. A knowledge of the degree of thermal equilibrium in plasmas is important for any serious plasma chemistry research program.

Usually, in plasma chemistry literature one distinguishes between "low,"-temperature and "high"-temperature chemistry of plasmas. A distinctive point of difference often cited is the accompanying nonpropagating electromagnetic field, which may be present as the agency supplying the energy needed to maintain the plasma or as the means of providing a confining wall, such as a magnetic field. In this chapter and in the chapters which follow we consider low-temperature plasma chemistry to include the reactions in plasmas with temperatures below 10^5 °K, that is, energies less than 10 eV per particle. High-temperature plasma chemistry is then concerned with reactions in plasmas at temperatures much greater than 10^5 °K. To be more specific, nuclear reactions in plasmas are discussed under the latter topic.

Often the major reason for using a plasma will be to achieve high temperatures in a chemical reaction, not as a reactant in the reaction itself. For this reason we shall examine the relation between energy and temperature for gases commonly used in plasmas and briefly refer to plasma heat-transfer literature. The dependence of energy on temperature (at equilibrium, 1 atm) is shown in Fig. 2 for some monatomic and diatomic gases. The diatomic molecules require 90 to 200 kcal $mole^{-1}$ to dissociate between 4000 and 10,000°K, while ionization requires 340 to 600 kcal $mole^{-1}$ between 10,000 and 30,000°K. The upper practical limit of flame temperatures is about
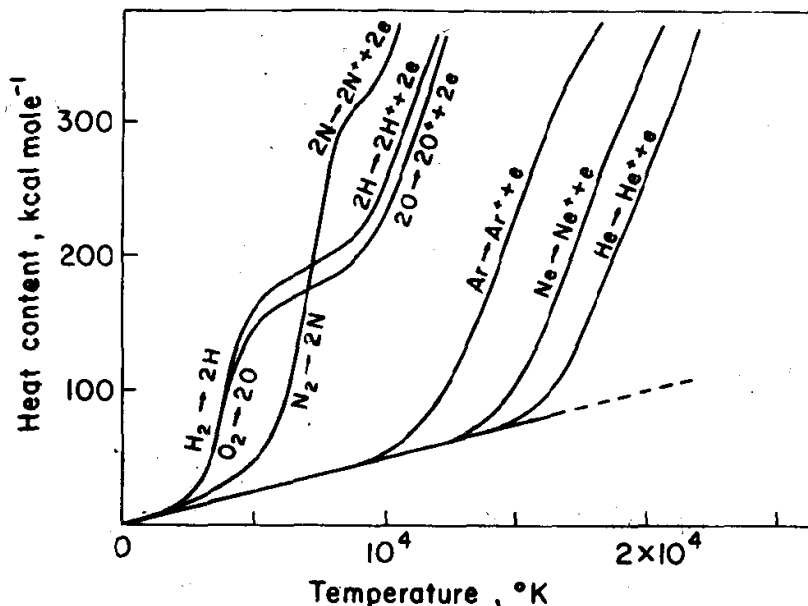

Figure 2   Heat content of gases commonly used in plasmas as a function of temperature at 1 atm pressure. [After T. B. Reed (4).]

3500°K, where molecules begin to dissociate, while the lower limit of plasma temperatures is about 10,000°K, since only at these temperatures is there enough ionization to carry the current that maintains the plasma. Most laboratory plasmas are heated electrically and, therefore, their temperatures will lie above the bottom end of the ionization curve, or above 10,000°K for the diatomic gases, but may be as low as 5000°K for some metal vapors.

Figure 2 also illustrates an important economic fact about the use of plasmas. In any process operated below 1000°K an air-fuel flame (~ 2000°K) or an oxygen-fuel flame (~ 3000°K) will have a high percentage of its energy available for the process. However, for a reaction occurring at 2500°K, for instance, only one sixth of the energy contained in an oxygen flame is available, and the rest must either be wasted or recovered in expensive heat exchangers. On the other hand, a plasma flame composed of atomic nitrogen at 10,000°K would have more than 90% of its energy available above 2500°K. This high energy efficiency may more than offset the economic advantage that combustion energy has over electrical energy; certainly this advantage will increase as electrical energy gets cheaper while fossil energy gets more expensive.

Heat transfer from plasmas depends on gaseous convection, electron transfer, and radiation. Plasma jets and electric arcs impinging on solid surfaces can produce very high heat-transfer rates. The heat-transfer intensity has been measured or estimated for a number of plasma devices, and the interested reader may find a summary of the results in the articles by Emmons (5) and Reed (4). Such information is sometimes useful to the plasma chemist, since it indicates temperature and enthalpy profiles and reaction times in plasma flows.

In principle, for both reactions within the bulk plasma and reactions of the plasma with the confining material walls, we shall be concerned with two distinct processes: (a) destruction of existing bonds, leading to creation of simpler molecules or free radicals and (b) formation of new bonds, resulting in the synthesis of bigger molecules.

Chemical bonds simply represent electron distributions between positively charged nuclei making up the cores of the atomic population of the molecule, mutually adjusted to yield maximum binding. These electron distributions will exhibit varying topologies for different molecules. Therefore, the nature of the agency supplying the energy needed to maintain the plasma will determine to some degree the efficiency with which particular bonds are broken or, conversely, the ease with which certain bonds can be created. A complication which must be accepted is that in any given type of reactor in which plasma reactions occur, there will usually be many different species which are simultaneously inducing the formation as well as destruction of bonds. Hence the net yield will be determined by the outcome of this competition.

Chemical synthesis which involves rearrangement of electron distributions to form new bonds (molecules) may frequently be achieved more efficiently in glow discharges at low pressures. However, sometimes a high yield can be obtained in spark discharges, and for particular chemical reactions the arc discharge may be most suitable. Again, the electromagnetic radiation quanttum (photon) may be the best means of achieving certain types of chemical or molecular syntheses.

Nuclear synthesis, on the other hand, involves the synthesis of heavier nuclei from lighter and simpler constituents by "fusion" reactions. The process is analogous to chemical synthesis of molecules from atoms or lighter molecules, and as in some chemical synthesis there is considerable interest in the energy release attending the reaction. However, nuclear synthesis can be achieved only at temperatures as high as 10^8–10^9 °K and therefore very high-temperature plasmas are required.

Although there is no strict isomorphism between molecular reactions and nuclear reactions, they are both describable in similar terms. The nucleus can be described in terms which very much resemble the description given an atom or molecule. That is, nuclear properties have been found to be almost completely explicable on the basis of the existence of a central field which localizes the neutrons and protons much the same as the nuclear electrical positive charge constrains and orders the motions of the surrounding electrons of atoms and molecules. Just as in atoms, in which there is a tendency to form shells of electrons, there is in the nucleus a similar tendency to form shells of both protons and neutrons. The problem of determining the kinetics of the nuclear reactions, like the chemical problem, is solved if the cross-section is found as a function of the relative velocities of the reactant particles. It must however be noted that chemical reactions correspond to energies per individual particle synthesis of the order of 1 eV and their cross-sections are of the order of 10^{-16} cm^2. In contrast nuclear reactions correspond to energies in the MeV range, and their cross-sections are of the order of 10^{-24} cm^2 only, with fusion collisions having still somewhat lower cross-sections.

III. LOW-TEMPERATURE PLASMA CHEMISTRY

A. General Observations

The particles present in a low-temperature plasma—electrons, ions, and neutrals—do not necessarily have the same temperature. A characteristic trend is that such differences become pronounced with decreasing pressure. Conversely, with high pressures the temperatures of the plasma particles tend to equilibrate.

Working temperatures ordinarily vary from near room temperatures to 10^4 °K for the heavy particles, atoms, and ions. For the electron component

the temperatures range from those descriptive of the heavy particles to upwards of 10^5 °K and more. (Pressures can run from vacuum values to hundreds of atmospheres.) Therefore, equilibration will lead to a considerable lowering of the electron temperature. If electrons are the means by which a certain reaction occurs, an increase in pressure can produce a deleterious effect on the net reaction yield. In other words, the effect of increasing pressure will lead to a greater frequency of energy exchange between the electrons, ions, and neutral species, and will tend to adjust the electron temperature closer to that of the heavy particles. The degree of cooling for electrons will be far greater than the heating of the heavy particles, since there will be, in a low-temperature plasma, a great excess of low-temperature neutrals and ions compared to electrons, and since each neutral molecule and ion may be capable of absorbing much more energy for a given temperature rise than the electrons. Thus with increasing pressure there will be an associated decrease in electron energy. If the electron temperature is greatly reduced, only few electrons will have the required energy of activation to carry out the formation of the required bonds, and the yield will thereby be diminished.

Increasing the system pressure may also tend to decrease the number concentration of electrons—this trend is readily understood when the kinetics of electron generation is defined. Ionization occurs when an electron colliding inelastically with a neutral species, drives out an electron, suffering at the same time a reduction of its own energy equal to the amount given to the ejected electron. The nonradiative reverse process, which predominantly accounts for electron-ion recombination, is that in which two electrons collide in the neighborhood of an ion. The electron with the reduced energy is simultaneously captured into the bound state of the neutral molecule. The latter is a three-body process, whereas ionization is a two-body process; the rates of both processes are proportional to the product of the number densities of the particles taking part in each. If the number densities of the particles taking part in each were to be scaled up, it is clear that the recombination rate would increase more rapidly than the ionization rate—hence the observation that the number concentration of electrons tends to reduce at the higher pressures.

Unfortunately, only a partial knowledge of the somewhat complicated pattern of low-temperature plasma chemistry is accessible to us. In addition to the component of plasma electrons, other species do not maintain good thermal contact with their associates. Molecules in excited vibrational levels, metastable electronic levels, and certain ionic species can, in special circumstances, be quite indifferent to environmental changes or, at times, excessively sensitive to such disturbances.

Compared to conventional chemistry, the characteristic departure which plasma chemistry shows is oversimplified when categorized as a failure of the

equilibrium. If two plasma states are superposed one on the other, the deviation from equilibrium will be altered in exceedingly complicated ways. Reaction rates do not run proportional to particle densities alone—this is simply the failure of Guldberg and Waage's mass action law. One should therefore anticipate that the concentration ratios of reactants and products in electrical discharges might differ very much from the values obtained in purely thermal reactors. This is not always the case. For example, in the oxidation of CO to CO_2 in an electrical discharge at low-current densities the concentration ratios obtained at room temperature can be shown to correspond to the ratios of reactants and products obtained in a purely thermal reactor at 3000 °K.

It has long been recognized that in electrical discharges the essential chemical nature of each type of molecule can be changed. For example, the normally inert noble gases can become quite active chemically. The reason for this is that if an electron, in colliding with a neutral, can throw a bound electron into a normally unpopulated shell, the latter can then be free to form chemical bonds with other atoms, that is, it is no longer compelled to exist in such a strongly localized bound state. It is therefore not too suprising that noble gases such as helium and argon readily oxidize in an electrical discharge. They can also be made to combine with a number of other elements and with each other. The compounds thus formed are not stable in the gaseous form and will decompose in the absence of the discharge. However, they can enter into the kinetics of some other reactions in the discharge, functioning very importantly as does a catalyst.

On the other hand, in atoms with nearly filled shells electron collisions may move electrons from deep-lying levels to populate the top vacant levels and thus, temporarily, create the appearance of chemical inertness.

All these considerations reaffirm the fact that one must examine plasma reactions individually to discover the relevant and significant principles which govern the kinetics of the process. Different modes of plasma generation alter relative populations of various plasma species in characteristically different ways, forcing one to conclude that different plasma types have the status of distinctly unique elements.

Before discussing the reactions that may occur in the bulk plasma and plasma chemical processing in general, we shall briefly refer to the reactions between plasma particles and electrode or wall materials of the plasma reactor.

B. Reactions with the Electrode and Wall Materials

1. *Cathode Interactions.* When positively charged ions moving down the electrical-field gradient collide with the cathode surface atoms, combinations