Ionization in High-Temperature Gases

Editor: KURT E. SHULER

Associate Editor: JOHN B. FENN

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PREFACE

This volume is based to a large extent on the Conference on Ions in Flames and Rocket Exhausts sponsored by the American Rocket Society in Palm Springs, California, October 10-12, 1962. A number of the papers presented at this meeting are included in this book. In addition, the editor solicited for inclusion in this volume several review papers from a number of experts in order to present to the prospective audience a fairly comprehensive and self-contained survey of the field. Thus, this book is intended as a report on, and as an authoritative reference source of, the present status of the field of ionization in high-temperature gaseous systems.

With the advent of space flight and space exploration and with the current research and development activities in plasma physics and magnetohydrodynamics, the subject of ionization in high-temperature gases has assumed an important place in the forefront of research. A perusal of the table of contents will indicate the wide scope of problems in which ionization, i. e., the production of free electrons and ions, plays an important role. To set the stage and to orient the reader, who will not necessarily be an expert in this field, we have provided in Section I two authoritative review articles which are concerned with the thermodynamics and the basic elementary processes of gaseous ionization. The information contained therein is basic to the more complex problems discussed in the subsequent sections.

The study of the mechanism and energetics of the elementary chemical reactions in flames, as detailed in the papers in Section II, has contributed greatly to our understanding of ionization in combustion systems. Among the many topics discussed in these papers are: chemi-ionization, i. e., the production of ions and electrons in nonequilibrium concentration through specific chemical reactions, the kinetics and thermodynamics of electron attachment and detachment reactions, electron-ion recombination reactions, and conductivity measurements in flames. The fundamental information obtained from these flame studies has provided us with a better understanding and control of the many complex phenomena in aerospace applications.

The study of shock waves and detonation waves also has furnished valuable information on the elementary processes of ionization in high-temperature systems. Of particular importance in the detonation wave research have been the interesting effects due to the interaction of the shock wave with the chemical reactions. In addition to these important basic research aspects, the study of ionization in shock and detonation waves is also of great practical importance in connection with supersonic flight, re-entry phenomena, and other aerospace developments. The recent research activities and the status of this field are reviewed in Section III.

The chemistry of ionization in rocket exhausts is considered in Section IV. From the basic point of view, one meets here again the complicated interplay between chemical reactions and hydrodynamics which gives rise to a number of interesting phenomena in the ionization in high-temperature reactive gas streams. From a more applied point of view it is of great importance to have this basic knowledge in order to understand and subsequently control the resulting electromagnetic effects which can cause serious interference with communication and guidance.

The papers in Section V are devoted to the problems of the production, control, and utilization of the free electrons produced in high-temperature ionization processes. For purposes of magnetohydrodynamic power production it is essential to have an electrically conducting working fluid such as, for instance, a weakly ionized plasma. Whereas in some of the earlier papers in this volume the emphasis might have been on the suppression of ionization, the emphasis in these studies is instead on the enhancement of ionization, with its concomitant increase in the concentration of free electrons, through the seeding of gases or through the use of specialized combustion techniques. The final two papers in this section are devoted to a most novel application of ionization, namely, the scattering and reflections of radio waves from high-altitude chemical plasma clouds. An important aspect of this research effort is again the generation of free electrons and the enhancement of their concentration.

The material presented in this volume in essence, then, summarizes much of our present knowledge in the field of ionization in high-temperature gaseous systems. As such, it stands as an impressive testimonial to the ingenuity and industriousness of the many active workers in this field, and to our increased understanding and knowledge over the past decade.

The editor would like to express at this point his appreciation to the many contributors for their wholehearted cooperation in the preparation of this volume. Particular thanks are due a number of authors who at the request of the editor, and on short notice, prepared contributions for inclusion in this book on subjects not covered during the conference. The editor also gratefully acknowledges the assistance of Dr. John B. Fenn, Princeton University, in the preparation of this volume. Finally he wishes to express his appreciation to Dr. Martin Summerfield, Series Editor, and Miss Ruth F. Bryans, Managing Editor,

Scientific Publications Department, of the AIAA, and members of her staff, for their help and guidance in bridging the gap from good intentions to actual completion.

Kurt E. Shuler
Assistant Director and Senior
Research Fellow
National Bureau of Standards
Washington, D. C.

August 5, 1963

CONTENTS

I
ELEMENTARY PROCESSES

THERMODYNAMICS AND ELEMENTARY PROCESSES OF GASEOUS IONS

R. Stephen Berry*

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Abstract

The thermodynamics and microscopic processes associated with ions in hot gases are surveyed. Processes are classified and discussed according to whether they are charge production, charge conserving or recombination processes. Emphasis is placed on specification of the important physical variables and magnitudes governing the various processes. An attempt is made to describe the present theoretical and experimental situation in each area, and to point out recently-solved and outstanding unsolved problems.

1. Introduction

This section is intended as an elementary survey and review of the conditions associated with the presence of ions in gases, and of the processes involved in their production and destruction. With as sweeping a topic as this, the discussion must necessarily be exceedingly selective and brief in treating any single subject. The material divides itself into three parts: the equilibrium conditions associated with gaseous ions, the microscopic processes associated with the production, destruction and reactions of ions, and the macroscopic transport properties of ionized gases.

This chapter is devoted only to the thermodynamics and microscopic phenomena, and omits discussion of the transport properties. Throughout, the principal aim will be the presentation of the physical basis of each phenomenon, its magnitude, and the main physical factors involved. An attempt will be made to discuss, in each case, the present state of experimental and theoretical work, but without any presumption of

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Submitted to AIAA May 1, 1963.

*Assistant Professor, Department of Chemistry; Alfred P. Sloan Fellow.

reviewing the literature in detail. Pertinent books and review articles are cited as often as possible. Current literature references are sparse, and the author must apologize at the outset to the many people working in this broad field whose contributions are not mentioned explicitly.

2. Equilibrium Conditions

The presence of gaseous ions and electrons under conditions of equilibrium is a phenomenon easily understood and one which lends itself to very straightforward and detailed computation. Our knowledge of atomic and molecular energy levels is very detailed; and, in the limiting case in which potential energies of ionic interaction are small compared with the kinetic energy of individual ions, we know from the theory of electrolytes the laws governing the equilibrium and transport properties. The condition of equilibrium is simply the requirement that the mass-action laws (or Saha equation, in the case of ions and electrons) be satisfied. If there are n independent reactions possible, then there are n equations stating the conditions that the chemical potential be stationary. Each of these has the form of an expression for an equilibrium constant:

$$K = \frac{\prod_{i=1}^{\ell} (Z_i/V)}{\prod_{j=1}^{m} (Z_j/V)} = \frac{\prod_{i=1}^{\ell} \nu_i \gamma_i}{\prod_{j=1}^{m} \nu_j \gamma_j} \qquad (2.1.)$$

where V is the volume, i refers to products (ℓ in number), j refers to each of the m reactants, Z_k is the partition function of the k^{th} species, ν_k is the number density of the k^{th} species and γ_k is its activity coefficient. The units of ν_i are those of V^{-1}.

When the partition Z_k are evaluated from atomic and molecular data, one can supply the necessary conditions of composition, such as total amount of material or amounts of specific species, and solve the equilibrium equations for the remaining concentrations. These concentrations naturally appear in the activity coefficients for a dilute plasma of equally charged ions,