PLASMA SCIENCE AND TECHNOLOGY

Herman V. Boenig

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Also by Herman V. Boenig

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Preface

This book describes applications of low-temperature plasmas to chemical reactions and, in greater detail, to polymers formed or treated in plasma. Both the mechanisms of polymerization of reactive plasma species and the structure of such polymers are discussed in the light of present knowledge. Separate chapters describe their properties and applications. In addition, modifications of material surfaces by a plasma environment are shown to alter their surface properties markedly either by enhanced crosslinking of polymer surfaces or by introduction into such surfaces of other atoms or groups. Implantation of ions into metal surfaces is also described in detail as a rapidly evolving technique that imparts important properties to metal surfaces.

The unique properties of such plasmas have offered opportunities for processes hitherto inaccessible; plasmas find use as membranes permitting reverse osmosis and have other applications in areas as varied as microcircuitry, integrated optics, etching, detoxification, and thin-layer deposition. Experiments have also demonstrated that in a plasma containing the elements of our earth's atmosphere, for example, Co_2, N_2, and H_2, building blocks for life on earth, such as amino acids, can be synthesized. In addition, we have seen that in an oxygen plasma, organic matter can be completely converted into carbon dioxide and water and that this technique is now considered for use in devices to clean polluted air and to convert waste products in such confined spaces as submarines and space capsules.

Both the complexity and number of chemical reactions and products involving a plasma environment point to the importance of an entirely new field in chemistry, as in physics, the field of plasma chemistry.

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1. A Brief History

The term "plasma" was first used by Irving Langmuir [1] in 1926 to describe the inner region of an electrical discharge. Later, the definition was broadened to define a state of matter in which a significant number of the atoms and/or molecules are electrically charged or ionized. The first form of plasma observed was the positive column of the glow discharge, in which an equal number of positive ions and electrons are present.

Plasmas differ greatly in many respects, depending on the parameters by which they are generally classified; these include the pressure, charged-particle density, and temperature. Furthermore, the boundary conditions as well as the presence of external electric and/or magnetic fields yield different forms of plasma. The broad definition of plasma as a collection of equal numbers of positive- and negative-charge carriers makes the subject area quite extensive. It does not imply any restriction as to the density of the charged particles, the presence of neutral species, the emission or absorption of electromagnetic radiation, or the motion of particles.

If the positive ions are fixed, as in a solid, and the electrons are mobile, the system may be referred to as solid-state plasma. Liquid plasmas exist in salt solutions in which the positive and negative ions move separately. In this treatise only plasmas in a gaseous state are considered, that is, in a state in which free electric charges can move through the gas, usually under the influence of an electric field, in which the gas is ionized. Langmuir made measurements by inserting small conducting probes into such plasmas. Much later, such "Langmuir probes" were used in rockets and satellites to make the first in situ measurements of ionospheric plasma [2]. In subsequent years such probes have been widely employed to measure ionospheric electron temperatures and densities.

The majority of the universe exists in a plasma state, including the stars, which are almost completely ionized because of their high temperatures. The stars are an example of an equilibrium plasma, in which the ionization is thermally induced and the temperatures of the neutral and charged species are in equilibrium. In laboratory experiments, such an equilibrium plasma is fairly uncommon, since laboratory techniques usually involve nonequilibrium processes, which maintain the ionization by raising some of the charged species to a higher temperature than the neutrals. The most common of these processes is the gas discharge, in which an electrical potential, applied across a gap, provides the selected excitation of the charged species. In the case where most of the ionization occurs by direct electron impact, rather than by thermal channels, the discharge is referred to as glow discharge. The electrical discharge is observed where a gas or vapor becomes electrically conducting. One of the earliest sources of this phenomenon appears to be W. Gilbert's *De magnete, magneticisque corporibus, et de magno magnete tellure*, published in 1600. Gilbert found that a charged conductor loses its charge when brought near a flame and that an electroscope becomes charged when it is connected to a flame. Coulomb [3], in 1785, was probably the first to observe that a charged metal sphere loses the greater part of its charge through the air and not through imperfect insulation. About 1800, Petroff [4] discovered the arc discharge. He observed that when the points of two pieces of charcoal connected to a battery were brought together and then drawn apart, a continuous discharge occurred in the air, forming an arc of light of brilliancy hitherto unknown. The arc persisted even when the air pressure was reduced. In the 1830s Faraday [5] discovered what he called a glow discharge at low gas pressure; the glow discharge consisted of a series of alternate luminous and dark zones that varied in length and color, being sometimes stationary and sometimes in motion in the form of striations. These phenomena occurred in tubes filled with air at a few mm of pressure while the discharge was maintained by a source of potential of about 1000 V. He also observed that the current can pass through a discharge tube filled with a gas at low pressure without exhibiting any luminosity at all. This he referred to as a dark discharge. These phenomena, that is, the dark discharge, the glow discharge, and the arc discharge, can conveniently be considered as the three fundamental types of continuous electric discharge. They are self-sustained, since they can be maintained without the support of an external ionizing agency.

In 1858 Plücker [6] found that a glow discharge at a pressure of 1/100 mm Hg emits cathode rays. The beam colors the gas along its path, and when it impinges on the glass wall of the discharge tube, a green fluorescent spot is produced. Eleven years later, Hittorf [7] observed that these cathode rays can be deflected into a magnetic field; and it was subsequently shown [8] that cathode rays are also deflected by an electric field. Crookes [9] stated in 1879 that "the phenomena in these exhausted tubes reveal to physical science a new world, a world where matter may exist in a fourth state." In 1887 Hertz [10] observed that light emitted by a spark caused an adjacent spark gap to break down more easily. One year later, Hallwachs [11] reported that a zinc plate irradiated with UV light becomes positively charged (as a result, we now know, of the emission of photoelectrons). It soon became evident that the cathode rays must have a mass much smaller than that of the lightest gas atoms, and they were considered particles of negative electricity, for which Stoney [12] proposed the name "electron." By the end of the 19th century it was firmly established that these particles carried a negative charge. In 1886 Goldstein [13] demonstrated the existence of rays of positive ions by passing these "canal rays" into an adjoining chamber through a hole in the cathode of a glow discharge. Subsequent work early in this century supplied additional information about the properties of beams of positive ions, a field of still continuing research.

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2. The Nature of Plasma

1. General

Plasma can be broadly defined as a system of electric neutrality composed of positive- and negative-charge carriers (see diagram below). The degree of ionization may range from small, as is the case for the reactions discussed in this treatise, to very high, as in the systems studied by physicists in areas such as nuclear reactions. Within these regions, gases may display a wide variety of physical and chemical properties entirely different from those encountered under normal conditions, thus pointing to Crookes's concept, mentioned earlier, of plasma as a fourth state of matter.

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A number of natural and man-made plasmas were mentioned in chapter 1. One condition for plasma is that it must always be neutral. Therefore, a more specific definition of a plasma is that it is an ensemble of positively and negatively charged particles arranged in such a manner as to shield externally and internally generated electrostatic fields. This electric neutrality is true only in a macroscopic sense. If attention is focused on one single charged particle within a plasma, such as a positive ion, its radial field will induce charge separation in its immediate vicinity. This causes electrons to be at-