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Introduction to Theoretical and Applied Plasma Chemistry

1.1. PLASMA AS THE FOURTH STATE OF MATTER

Although the term *chemistry* in the title of the book does not require a special introduction, the term *plasma* probably does. Plasma is an ionized gas, a distinct fourth state of matter. "Ionized" means that at least one electron is not bound to an atom or molecule, converting the atoms or molecules into positively charged ions. As temperature increases, molecules become more energetic and transform matter in the sequence: solid, liquid, gas, and finally plasma, which justifies the title "fourth state of matter."

The free electric charges – electrons and ions – make plasma electrically conductive (sometimes more than gold and copper), internally interactive, and strongly responsive to electromagnetic fields. Ionized gas is usually called plasma when it is electrically neutral (i.e., electron density is balanced by that of positive ions) and contains a significant number of the electrically charged particles, sufficient to affect its electrical properties and behavior. In addition to being important in many aspects of our daily lives, plasmas are estimated to constitute more than 99% of the visible universe.

The term *plasma* was first introduced by Irving Langmuir (1928) because the multi-component, strongly interacting ionized gas reminded him of blood plasma. Langmuir wrote: "Except near the electrodes, where there are sheaths containing very few electrons, the ionized gas contains ions and electrons in about equal numbers so that the resultant space charge is very small. We shall use the name **plasma** to describe this region containing balanced charges of ions and electrons." There is usually not much confusion between the fourth state of matter (plasma) and blood plasma; probably the only exception is the process of plasma-assisted blood coagulation, where the two concepts meet.

Plasmas occur naturally but also can be effectively man-made in laboratory and in industry, which provides opportunities for numerous applications, including thermonuclear synthesis, electronics, lasers, fluorescent lamps, and many others. To be more specific, most computer and cell-phone hardware is made based on plasma technologies, not to forget about plasma TV. In this book, we are going to focus on fundamental and practical aspects of plasma applications to chemistry and related disciplines, which probably represent the major part of complete plasma science and engineering.

Plasma is widely used in practice. Plasma offers three major features that are attractive for applications in chemistry and related disciplines: (1) temperatures of at least some plasma components and energy density can significantly exceed those in conventional chemical technologies, (2) plasmas are able to produce very high concentrations of energetic and chemically active species (e.g., electrons, ions, atoms and radicals, excited states, and different wavelength photons), and (3) plasma systems can essentially be far from thermodynamic equilibrium, providing extremely high concentrations of the chemically active species and

Figure 1–1. Benjamin Franklin's first experiments with the atmospheric plasma phenomenon of lightning.

keeping bulk temperature as low as room temperature. These plasma features permit significant intensification of traditional chemical processes, essential increases of their efficiency, and often successful stimulation of chemical reactions impossible in conventional chemistry.

Plasma chemistry today is a rapidly expanding area of science and engineering, with applications widely spread from micro-fabrication in electronics to making protective coatings for aircrafts, from treatment of polymer fibers and films before painting to medical cauterization for stopping blood and wound treatment, and from production of ozone to plasma TVs. Let us start the long journey to theoretical and applied plasma chemistry by getting acquainted with the major natural and man-made plasmas.

1.2. PLASMA IN NATURE AND IN THE LABORATORY

Plasma comprises the majority of the universe: the solar corona, solar wind, nebula, and Earth's ionosphere are all plasmas. The best known natural plasma phenomenon in Earth's atmosphere is lightning. The breakthrough experiments with this natural form of plasma were performed long ago by Benjamin Franklin (Fig. 1–1), which probably explains the special interest in plasma research in Philadelphia, where the author of the book works at the Drexel Plasma Institute (Drexel University).

At altitudes of approximately 100 km, the atmosphere no longer remains non-conducting due to ionization and formation of plasma by solar radiation. As one progresses further into near-space altitudes, the Earth's magnetic field interacts with charged particles streaming from the sun. These particles are diverted and often become trapped by the Earth's magnetic field. The trapped particles are most dense near the poles and account for the aurora borealis (Fig. 1–2). Lightning and the aurora borealis are the most common natural plasmas observed on Earth.

Natural and man-made plasmas (generated in gas discharges) occur over a wide range of pressures, electron temperatures, and electron densities (Fig. 1–3). The temperatures of

Figure 1–2. Aurora borealis.

man-made plasmas range from slightly above room temperature to temperatures comparable to the interior of stars, and electron densities span over 15 orders of magnitude. Most plasmas of practical significance, however, have electron temperatures of 1–20 eV, with electron densities in the range 10^6–10^{18} cm^{-3}. (High temperatures are conventionally expressed in electron volts; 1 eV approximately equals 11,600 K.)

Not all particles need to be ionized in plasma; a common condition in plasma chemistry is for the gases to be only partially ionized. The ionization degree (i.e., ratio of density of major charged species to that of neutral gas) in the conventional plasma–chemical systems is in the range 10^{-7}–10^{-4}. When the ionization degree is close to unity, such plasma is called **completely ionized plasma**. Completely ionized plasmas are conventional for thermonuclear plasma systems: tokomaks, stellarators, plasma pinches, focuses, and so on. Completely ionized plasma and related issues of nuclear fusion and space plasmas are the subject of several books, in particular those of Bittencourt (2004) and Chen (2006); thermonuclear and space plasmas are not the focus of this book. When the ionization degree is low, the plasma is called **weakly ionized plasma**, which is the main focus of plasma chemistry and this book.

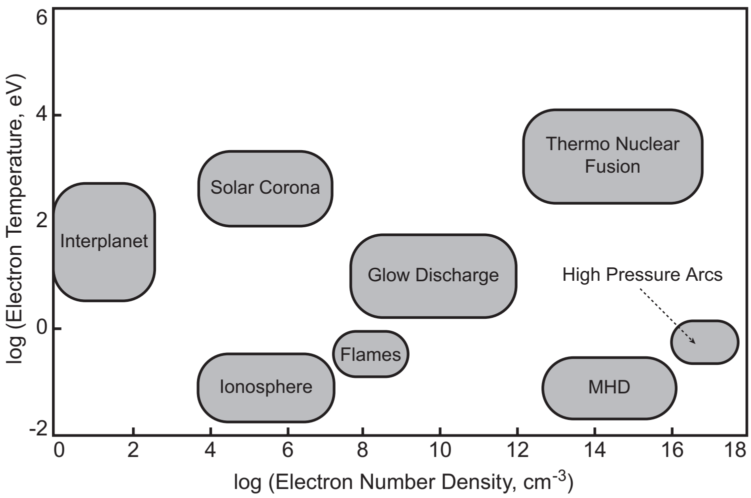

Figure 1–3. Plasma temperatures and densities.

Both natural and man-made laboratory plasmas are quasi-neutral, which means that concentrations of positively charged particles (positive ions) and negatively charged particles (electrons and negative ions) are well balanced. Langmuir was one of the pioneers who studied gas discharges and defined plasma to be a region not influenced by its boundaries. The transition zone between the plasma and its boundaries was termed the plasma **sheath**. The properties of the sheath differ from those of the plasma, and these boundaries influence the motion of the charged particles in this sheath. The particles form an electrical screen for the plasma from influences of the boundary.

1.3. PLASMA TEMPERATURES: THERMAL AND NON-THERMAL PLASMAS

As in any gas, temperature in plasma is determined by the average energies of the plasma particles (neutral and charged) and their relevant degrees of freedom (translational, rotational, vibrational, and those related to electronic excitation). Thus, plasmas, as multi-component systems, are able to exhibit multiple temperatures. In electric discharges common for plasma generation in the laboratory, energy from the electric field is first accumulated by the electrons between collisions and, subsequently, is transferred from the electrons to the heavy particles.

Electrons receive energy from the electric field during their mean free path and, during the following collision with a heavy particle, lose only a small portion of that energy (because electrons are much lighter than the heavy particles). That is why the electron temperature in plasma is initially higher than that of heavy particles. Subsequently, collisions of electrons with heavy particles (Joule heating) can equilibrate their temperatures, unless time or energy are not sufficient for the equilibration (such as in coronas and pulsed discharges) or there is an intensive cooling mechanism preventing heating of the entire gas (such as in wall-cooled low-pressure discharges).

The temperature difference between electrons and heavy neutral particles due to Joule heating in the collisional weakly ionized plasma is conventionally proportional to the square of the ratio of the electric field (E) to the pressure (p). Only in the case of small values of E/p do the temperatures of electrons and heavy particles approach each other. Thus, this is a basic requirement for **local thermodynamic equilibrium** (LTE) in plasma. Additionally, LTE conditions require chemical equilibrium as well as restrictions on the gradients. The LTE plasma follows the major laws of equilibrium thermodynamics and can be characterized by a single temperature at each point of space. Ionization and chemical processes in such plasmas are determined by temperature (and only indirectly by the electric fields through Joule heating). The quasi-equilibrium plasma of this kind is usually called **thermal plasma**. Thermal plasmas in nature can be represented by solar plasma (Fig. 1–4).

Numerous plasmas exist very far from the thermodynamic equilibrium and are characterized by multiple different temperatures related to different plasma particles and different degrees of freedom. It is the electron temperature that often significantly exceeds that of heavy particles ($T_e \gg T_0$). Ionization and chemical processes in such non-equilibrium plasmas are directly determined by electron temperature and, therefore, are not so sensitive to thermal processes and temperature of the gas. The non-equilibrium plasma of this kind is usually called **non-thermal plasma**. An example of non-thermal plasmas in nature is the aurora borealis (Fig. 1–2).

Although the relationship between different plasma temperatures in non-thermal plasmas can be quite sophisticated, it can be conventionally presented in the collisional weakly ionized plasmas as $T_e > T_v > T_r \approx T_i \approx T_0$. Electron temperature ($T_e$) is the highest in the system, followed by the temperature of vibrational excitation of molecules (T_v). The lowest temperature is usually shared in plasma by heavy neutrals (T_0, temperature of translational

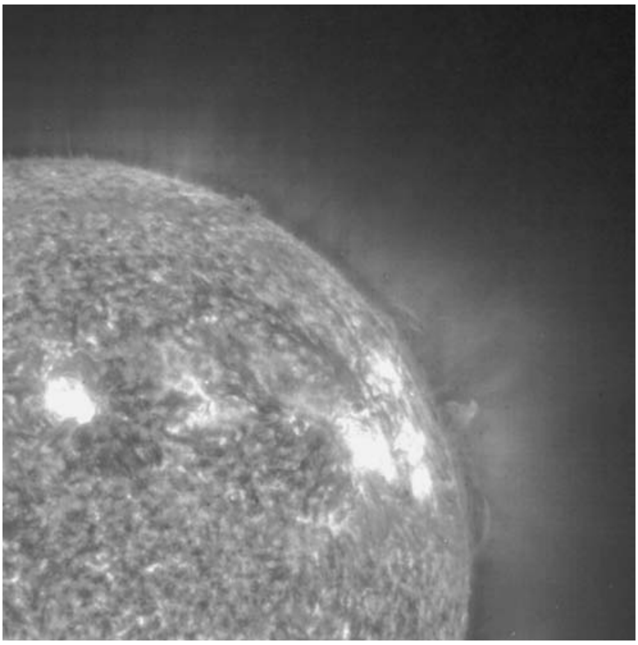

Figure 1–4. Solar plasma.

degrees of freedom or simply gas temperature), ions (T_i), as well as rotational degrees of freedom of molecules (T_r). In many non-thermal plasma systems, electron temperature is about 1 eV (about 10,000 K), whereas the gas temperature is close to room temperature.

Non-thermal plasmas are usually generated either at low pressures or at lower power levels, or in different kinds of pulsed discharge systems. The engineering aspects, and application areas are quite different for thermal and non-thermal plasmas. Thermal plasmas are usually more powerful, whereas non-thermal plasmas are more selective. However, these two very different types of ionized gases have many more features in common and both are plasmas.

It is interesting to note that both thermal and non-thermal plasmas usually have the highest temperature (T_e in one case, and T_0 in the other) on the order of magnitude of 1 eV, which is about 10% of the total energy required for ionization (about 10 eV). It reflects the general rule found by Zeldovich and Frank-Kamenetsky for atoms and small molecules in chemical kinetics: the temperature required for a chemical process is typically about 10% of the total required energy, which is the Arrhenius activation energy. A funny fact is that a similar rule (10%) can usually be applied to determine a down payment to buy a house or a new car. Thus, the plasma temperatures can be somewhat identified as the down payment for the ionization process.

1.4. PLASMA SOURCES FOR PLASMA CHEMISTRY: GAS DISCHARGES

Plasma chemistry is clearly the chemistry organized in or with plasma. Thus, a plasma source, which in most laboratory conditions is a gas discharge, represents the physical and engineering basis of the plasma chemistry. For simplicity, an electric discharge can be viewed as two electrodes inserted into a glass tube and connected to a power supply. The tube can be filled with various gases or evacuated. As the voltage applied across the two

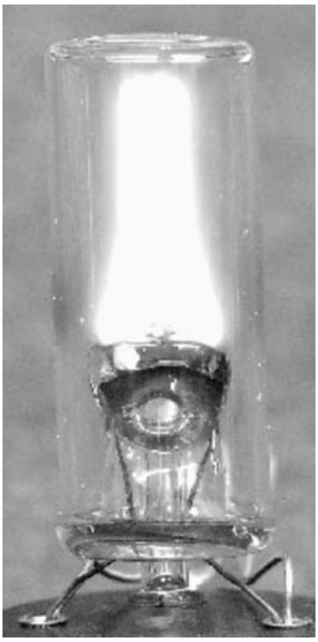

Figure 1–5. Glow discharge.

electrodes increases, the current suddenly increases sharply at a certain voltage required for sufficiently intensive electron avalanches. If the pressure is low, on the order of a few torrs, and the external circuit has a large resistance to prohibit a large current, a glow discharge develops. This is a low-current, high-voltage discharge widely used to generate non-thermal plasma. A similar discharge is known by everyone as the plasma source in fluorescent lamps. The glow discharge can be considered a major example of low-pressure, non-thermal plasma sources (see Fig. 1–5).

A non-thermal corona discharge occurs at high pressures (including atmospheric pressure) only in regions of sharply non-uniform electric fields. The field near one or both

Figure 1–6. Corona discharge.

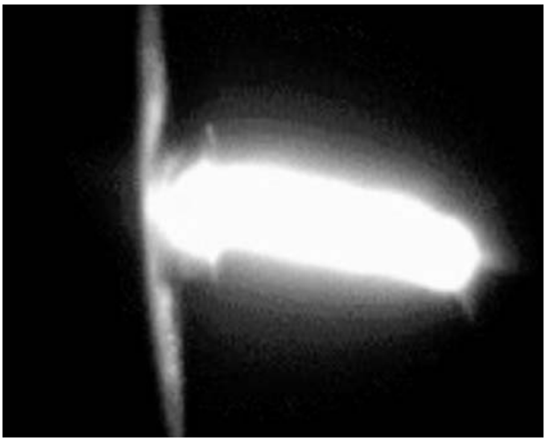

Figure 1–7. Arc discharge.

electrodes must be stronger than in the rest of the gas. This occurs near sharp points, edges, or small-diameter wires, which tend to be low-power plasma sources limited by the onset of electrical breakdown of the gas. However, it is possible to circumvent this restriction through the use of pulsating power supplies. Electron temperature in the corona exceeds 1 eV, whereas the gas remains at room temperature. The corona discharges are, in particular, widely applied in the treatment of polymer materials: most synthetic fabrics applied to make clothing have been treated before dyeing in corona-like discharges to provide sufficient adhesion. The corona discharge can be considered a major example of an atmospheric pressure non-thermal plasma source (see Fig. 1–6).

If the pressure is high, on the order of an atmosphere, and the external circuit resistance is low, a thermal arc discharge can be organized between two electrodes. Thermal arcs usually carry large currents, greater than 1 A at voltages of the order of tens of volts. Furthermore, they release large amounts of thermal energy at very high temperatures often exceeding 10,000 K. The arcs are often coupled with a gas flow to form high-temperature plasma jets. The arc discharges are well known not only to scientists and engineers but also to the general public because of their wide applications in welding devices. The arc discharge can be considered a major example of thermal plasma sources (see Fig. 1–7).

Between other electric discharges widely applied in plasma chemistry, we should emphasize that non-equilibrium, low-pressure radiofrequency discharges play the key roles in sophisticated etching and deposition processes of modern micro-electronics, as well as in treatment of polymer materials. More and more chemical processes have been organized recently in gliding arc discharges (powerful generators of non-equilibrium atmospheric pressure plasma), especially with plasma stabilization in reverse vortex "tornado" flow (see Fig. 1–8). The gliding arc "tornado" discharges provide a unique opportunity of combining the high power typical for arc discharges with the relatively high level of non-equilibrium typical for non-thermal atmospheric pressure discharges.

Between "non-traditional" but very practically interesting discharges, we can point out the non-thermal, high-voltage, atmospheric-pressure, floating-electrode dielectric barrier discharge (FE-DBD), which can use the human body as a second electrode without damaging the living tissue. Such a discharge obviously provides very interesting opportunities for direct plasma applications in biology and medicine (Fig. 1–9). Major discharges applied in plasma chemistry are to be discussed in Chapter 4. More detailed information on the subject can be found in special books focused on plasma physics and engineering, for example those of Roth (1995) and Fridman and Kennedy (2004).

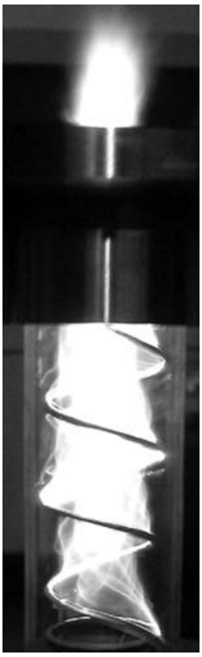

Figure 1–8. Gliding arc discharge stabilized in the reverse vortex ("tornado") gas flow.

1.5. FUNDAMENTALS OF PLASMA CHEMISTRY: MAJOR COMPONENTS OF CHEMICALLY ACTIVE PLASMA AND MECHANISMS OF PLASMA-CHEMICAL PROCESSES

Chemically active plasma is a multi-component system highly reactive due to large concentrations of charged particles (electrons, negative and positive ions), excited atoms and molecules (electronic and vibrational excitation make a major contribution), active atoms and radicals, and UV photons. Each component of the chemically active plasma plays its own specific role in plasma-chemical kinetics. Electrons, for example, are usually first to receive the energy from an electric field and then distribute it between other plasma components and specific degrees of freedom of the system. Changing parameters of the electron gas (density, temperature, electron energy distribution function) often permit control and optimization of plasma-chemical processes.

Ions are charged heavy particles, that are able to make a significant contribution to plasma-chemical kinetics either due to their high energy (as in the case of sputtering and reactive ion etching) or due to their ability to suppress activation barriers of chemical reactions. This second feature of plasma ions results in the so-called ion or plasma catalysis, which is particularly essential in plasma-assisted ignition and flame stabilization, fuel

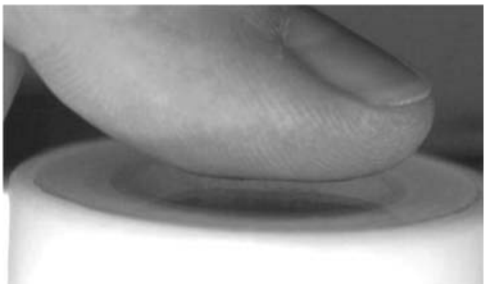

Figure 1–9. Floating-electrode dielectric barrier discharge (FE-DBD) with a finger as a second electrode.

conversion, hydrogen production, exhaust gas cleaning, and even in the direct plasma treatment of living tissue.

The vibrational excitation of molecules often makes a major contribution to plasma-chemical kinetics because the plasma electrons with energies around 1 eV primarily transfer most of the energy in such gases as N_2, CO, CO_2, H_2, and so forth into vibrational excitation. Stimulation of plasma-chemical processes through vibrational excitation permits the highest values of energy efficiency to be reached; see the example with CO_2 dissociation in the next section. Electronic excitation of atoms and molecules can also play a significant role, especially when the lifetime of the excited particles is quite long (as in the case of metastable electronically excited atoms and molecules). As an example, we can mention plasma-generated metastable electronically excited oxygen molecules $O_2(^1\Delta_g)$ (singlet oxygen), which effectively participate in the plasma-stimulated oxidation process in polymer processing, and biological and medical applications.

The contribution of atoms and radicals is obviously significant. As an example, we can point out that O atoms and OH radicals effectively generated in atmospheric air discharges which play a key role in numerous plasma-stimulated oxidation processes. Plasma-generated photons play a key role in a wide range of applications, from plasma light sources to UV sterilization of water.

Plasma is not only a multi-component system, but often a very non-equilibrium one (see Section 1.3). Concentrations of the active species described earlier can exceed those of quasi-equilibrium systems by many orders of magnitude at the same gas temperature. The successful control of plasma permits chemical processes to be directed in a desired direction, selectively, and through an optimal mechanism. Control of a plasma-chemical system requires detailed understanding of elementary processes and the kinetics of the chemically active plasma. The major fundamentals of plasma physics, elementary processes in plasma, and plasma kinetics are to be discussed in Chapters 2 and 3; more details on the subject can be found in Fridman and Kennedy (2004).

1.6. APPLIED PLASMA CHEMISTRY

Applications of plasma technologies today are numerous and involve many industries. High-energy efficiency (energy cost with respect to the minimum determined by thermodynamics), high specific productivity (productivity per unit volume of reactor), and high selectivity may be achieved in plasmas for a wide range of chemical processes. As an example, for CO_2 dissociation in non-equilibrium plasma under supersonic flow conditions, it is possible to selectively introduce up to 90% of the total discharge power in CO production when the vibrational temperature is about 4000 K and the translational temperature is only about 100 K. The specific productivity of such a supersonic reactor achieves 1,000,000 L/h, with power levels up to 1 MW. This plasma process has been examined for fuel production on Mars, where the atmosphere mostly consists of CO_2. On the Earth, it was applied as a plasma stage in a two-step process for hydrogen production from water.

As mentioned in the previous section, the key point for practical use of any chemical process in a particular plasma system is to find the proper regime and optimal plasma parameters among the numerous possibilities intrinsic to systems far from thermodynamic equilibrium. In particular, it is desired to provide high operating power for the plasma chemical reactor together with a high selectivity of energy input while maintaining non-equilibrium plasma conditions. Thermal plasma generators have been designed for many diverse industrial applications covering a wide range of operating power levels from less than 1 kW to over 50 MW. However, in spite of providing sufficient power levels, these generators are not well adapted to the purposes of plasma chemistry, where selective treatment of reactants and high efficiency are required. The main drawback of using thermal plasmas for plasma-chemical applications are that the reaction media become overheated when energy is uniformly consumed by the reagents into all degrees of freedom and, hence, high-energy consumption is required to provide special quenching of the reagents. Because of these drawbacks, the energy efficiency and selectivity of such systems are rather small (only a few of many thermal plasma-chemical processes developed in the first decades of the 20th century remain, e.g., the production of acetylene and other valuable chemicals from light hydrocarbons in Germany).

Recently, energy-efficient and powerful plasma-chemical systems have been developed based on microwave discharges. The skin effect in this case permits simultaneous achievement of a high level of electron density and a high electric field (and hence a high electron temperature as well) in the relatively cold gas. Microwave plasma technology permits dense ($n_e = 10^{13}$ cm^{-3}) non-equilibrium plasmas to be generated (T_e = 1–2 eV, T_v = 3000–5000 K, T_0 = 800–1500 K, and for supersonic flow $T_n \leq 150$ K) at pressures up to 200–300 torr and at power levels reaching 1 MW. Similar plasma parameters can be achieved in recently developed gliding arc discharges (see Fig. 1–8). These energy-effective, non-equilibrium but at the same time powerful plasma systems are optimal for fuel conversion and hydrogen production applications, where minimization of electric energy cost should be achieved together with very high productivities of the process.

Most of the book considers specific plasma applications (Chapters 5–12), widely spread from etching and chemical vapor deposition in micro-electronics to thermal spray coatings; from plasma metallurgy to the production of ozone; from plasma ignition and stabilization of flames to the treatment of synthetic fabrics and other polymer materials; from plasma TVs to sterilization of water and air streams; and from plasma treatment of exhaust gases to direct plasma treatment of burns, ulcers, and other skin diseases. Each plasma process obviously requires understanding of its mechanism, development of the most relevant discharge system, and choice of the most optimal plasma regime. These factors make the journey through applied plasma chemistry not only interesting and exciting but also somewhat long.

1.7. PLASMA AS A HIGH-TECH MAGIC WAND OF MODERN TECHNOLOGY

In many practical applications, plasma technologies compete with other approaches and successfully find their specific niche in modern industry. Such a situation takes place, for example, in thermal plasma deposition of protective coatings, in plasma stabilization of flames, in plasma conversion of fuels, in plasma light sources, in plasma cleaning of exhaust gases, in plasma sterilization of water, and so on. All these plasma technologies are practically interesting, commercially viable, and generally make an important contribution to the development of our society.

The most exciting applications of plasma, however, are related not to the aforementioned technologies but to those which actually have no analogies and no (or almost no) competitors. A good relevant example is plasma applications in micro-electronics, such as etching deep trenches (0.2 μm wide and 4 μm deep) in single crystal silicon, which is so important in the fabrication of integrated circuits. Capabilities of plasma processing in micro-electronics are extraordinary and unique. We probably would not have computers and cell phones like we have now without plasma processing. When all alternatives fail, plasma can still be utilized; plasma chemistry in this case plays the role of the high-tech magic wand of modern technology.

Among other examples, when plasma abilities are extraordinary and unique, we can point out plasma production of ozone where no other technologies are able to challenge plasma for more than 100 years, thermonuclear plasma as a major future source of energy, and low-temperature fuel conversion where hydrogen is produced without CO_2 exhaust, which is