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Cold plasma chemistry and diagnostics

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ABSTRACT

This paper gives an overview of the main chemical processes which take place in cold plasmas generated in glow discharges, both in the gas phase and at the surfaces in contact with the plasma. Illustrative examples are provided where the relevance of different processes is evinced. Most common plasma characterization techniques and their recent improvements are also presented briefly.

1. Introduction

Cold plasmas, produced mainly in electric glow discharges, are of great interest in a large number of scientific and technological fields [1–3]. In cold plasmas, ionization and dissociation of molecular precursors, initiated by collisions between free electrons and gas phase species, are followed by a great variety of processes that lead to special chemical conditions, very suitable for thin film growth, surface conditioning, biomaterials disinfection, energy saving lamps, laser sources, etc. [4]. Glow discharges can also simulate the border conditions of plasmas generated in fusion reactors [5]. In addition, they are very useful to produce radicals, ions and excited states, unstable under ordinary conditions, whose study can contribute to the understanding of the generation of similar compounds in the interstellar space and in the ionospheres of some planets [6].

The complex kinetics of cold molecular plasmas is difficult to disentangle, since they host a great deal of different species, with characteristic concentrations and lifetime scales spanning many orders of magnitude. Understanding the very diverse processes involved in these plasmas, both in homogeneous and heterogeneous reactions, needs basic reference data, including cross-sections, rate coefficients, sticking probabilities and so on, often unavailable. Therefore, a great effort and a variety of experimental and modelling techniques are currently devoted to the characterization of these systems.

Experimental diagnosis of glow discharges relies mainly on the use of mass spectrometry, spectroscopic techniques and electrical probes [4,7]. The development of particular methods for the sensitive detection of transient species, which play a key role in the plasma chemistry, is an active research field. Comparison of experimental results with theoretical models allows a better understanding of these systems and, as a result, an improvement in their applications.

In this work, the main kinetic processes taking place in cold plasmas generated in glow discharges and the methods most frequently used for plasma diagnostic will be discussed. Initially, we will see the processes that lead to plasma generation and the mechanisms that follow plasma ignition, largely responsible for its high chemical reactivity, even at room temperatures. Then, a short description of the experimental techniques presently available to study the different species involved is included. Finally, some cases, based mostly on our own work, will exemplify the relevance of different key processes.

2. Cold plasma chemistry

2.1. Plasma generation in glow discharges

Cold plasmas are plasmas with a low ionization degree, far from thermal equilibrium, where the electron temperatures (T_e) are much higher than the gas temperatures (T_{gas}). They show high stability and occur most commonly at low pressures.

Glow discharges are produced either by direct current, radio-frequency or microwave sources, where free electrons are accelerated and gain kinetic energy efficiently from the electromagnetic field. This energy is exchanged easily through elastic collisions with other electrons, giving rise typically to Maxwellian-like electron energy distributions (EED). However, the proportion of energy

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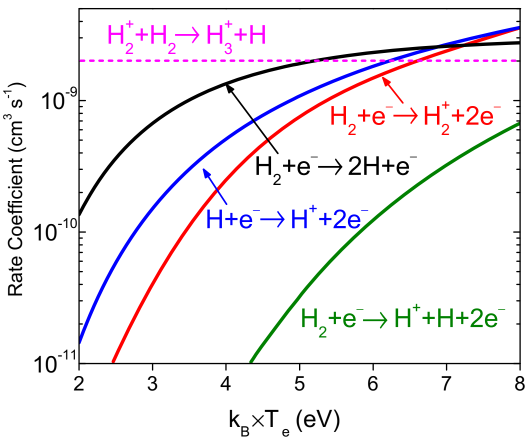

Fig. 1. Rate coefficients for relevant homogeneous reactions in H_2 plasmas, taken from the expressions given in Ref. [8].

transferred from one electron to a much heavier ion or neutral in each elastic collision is very low, smaller than four times the mass ratio between the electron and the other body. The average kinetic energy transfer increases with the number of collisions, i.e. with growing gas pressure.

Within the high energy tail of the EED, those electrons with higher energies than the ionization threshold of the precursors can ionize them liberating new free charges that compensate wall losses and neutralizations in the gas phase. These additional charges are essential to maintain the plasma stability. Glow discharges are stable over relatively broad pressure ranges, although the precise limits depend on the characteristic dimensions of the discharge. At the lowest pressures, electrons might gain much energy between collisions and enhance their ionization capability, but their collisions with neutrals are too scarce to generate sufficient new free charges, and the plasma extinguishes. At the highest pressure limits, the average gain of electron energy between collisions is not enough to compensate previous energy losses and to reach the ionization threshold. Then, the plasma becomes unstable and inhomogeneous, with tendency to arching.

2.2. Main gas phase reactions

Besides ionization, primary processes by electron impact on atoms and molecules are molecular dissociation and excitation to upper energy levels. Ionizations and dissociations require threshold energies of ~5–20 eV. Above these thresholds, the cross-sections increase with electron energy upto ~50–100 eV, decreasing smoothly afterwards. The electron velocity, times the cross-section, integrated along the whole velocity range, gives the rate coefficient, k, for each reaction. Fig. 1 displays the k dependences on T_e ($k = a \times k_B T_e b \times e^{-c/k_B T_e}$), for some rate coefficients involved in H_2 plasmas [8], assuming Maxwellian EED. For $k_B T_e \sim 2–8$ eV, typical of glow discharges, $k \sim 10^{-10}–10^{-9}$ cm^3 s^{-1} are commonly found. The electron densities, N_e, span usually a range from 10^9 to 10^{11} cm^{-3}; this means that, without any recovery process, precursors would be totally ionized or dissociated within characteristic times ($\tau = k \times N_e$) of tenths of seconds.

Excitations require discrete energy values of some eV to populate electronic upper levels, and tenths or hundredths of eV for vibrational or rotational excitations, respectively. Spontaneous emission from excited levels provides one of the most characteristic properties of plasmas: light radiation, and allows the identification of many species through their spectral analysis.

Selective losses of electron energies by ionization, dissociation and excitation can change the EED and move it away from a Maxwellian distribution.

Ions, atoms and radicals in ground or excited states liberated by the former processes are extremely reactive species, able to undergo secondary reactions at room temperature, which efficiently transform the plasma precursors into other products [9], or interact with the surrounding walls, changing the surface conditions. Their lifetimes in the plasma are very short, roughly, $\sim 10^{-3}–10^{-2}$ s for atoms and radicals and $\sim 10^{-7}–10^{-6}$ s for ions [10], since they recombine or neutralize very quickly; and their steady state concentrations are several orders of magnitude lower than those of stable species (Fig. 2). One exception to this rule is that the concentration of radicals and atoms can be unusually high in discharge chambers made from materials with a low coefficient for heterogeneous surface recombination [11–13]. The lifetimes of excited states extend $\sim 10^{-3}–10^{-9}$ s, depending on their transition probabilities and quenching cross-sections. Long lived excited states display higher populations than those which decay faster, leading to partial temperatures of some thousands of Kelvin (assuming Boltzmann distributions). Ions at the plasma sheath are accelerated in the electric field between the glow and the reactor surfaces, gaining energies up to tens of eV in RF discharges with dominant inductive coupling (high power, H mode) or MW discharges, and hundreds of eV in RF discharges with dominant capacitive coupling (low power, E mode) or, as well, when reaching a grounded cathode in DC reactors. These energies enhance markedly the effectiveness of ion collisions on the surfaces.

In the gas phase, bimolecular reactions with no energy barrier between transients and stable molecules predominate largely over other reactions. Their cross-sections decrease typically with collision energy as $E^{-1/2}$ (Langevin behaviour), but the relative velocity between the colliding particles is proportional to $E^{1/2}$. Then, the resulting rate coefficients are independent on T_{gas}, often with values $k > 10^{-10}$ cm^3 s^{-1} for reactions involving radicals, and $k > 10^{-9}$ cm^3 s^{-1} for ions. For example, $k = 2 \times 10^{-9}$ cm^3 s^{-1} for the process $H_2^+ + H_2 \rightarrow H_3^+ + H$ (Fig. 1). Electron impact dissociative neutralizations like $H_3^+ + e^- \rightarrow 3H$ (or $H_2 + H$) have even larger coefficients ($k \sim 10^{-7}–10^{-8}$ cm^3 s^{-1}), and can be very important in space chemistry; nevertheless, they are irrelevant in glow discharges as compared with wall neutralizations.

In bimolecular reactions with an energy barrier, the rate coefficients decrease exponentially with T_{gas} (Arrhenius' like dependence) and display small values ($k < 10^{-12}$ cm^3 s^{-1}), even at some thousands of Kelvin. So, although usually important in chemical reactors at high temperatures, they can be disregarded in cold plasma kinetics. Exothermic association reactions like $H + H \rightarrow H_2$ are not possible without a third body, which takes away the excess energy of molecular formation. However, gas phase reactions

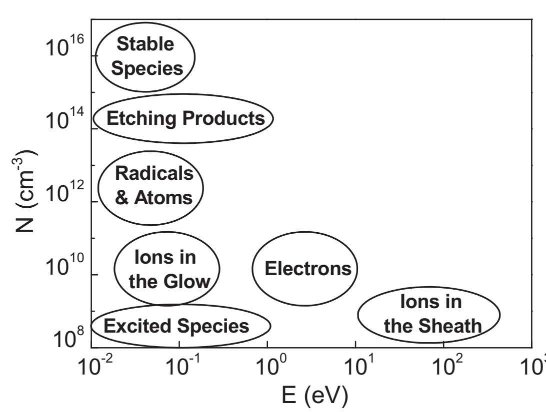

Fig. 2. Typical concentrations and energies of different species generated in glow discharges.