Small Molecule Ion Chemistry in ITER

J. Brian A. Mitchell, S. Carles, J.L. LeGarrec
Institut de Physique de Rennes
UMR du CNRS No. 6251
Université de Rennes I
35042, Rennes, France
mitchell@univ-rennes1.fr

Abstract. The new ITER reactor will have special problems with heat loads on exposed plasma surfaces. A good knowledge of the plasma chemistry is essential to be able to predict these heat loads and to find efficient ways of cooling the plasma near these surfaces. This paper addresses the data needs for light element reactions with particular emphasis on electron impact reactions.

1. Introduction
The International Thermonuclear Experimental Reactor ITER [1] is beginning construction at Cadarache in the south of France. This is an enormous project that is scheduled to begin operation after 2019 and the first use of tritium fuel to achieve thermonuclear ignition, is scheduled for after 2027. The technological challenges facing this experimental machine are daunting and successful operation will require amongst other things, a good knowledge of the atomic and molecular processes near the walls of the reactor and in the divertor region. A special issue of Nuclear Fusion, published in 2007 [1] gives an in-depth analysis of the technological and scientific issues involved in the design of ITER. One of the key engineering problems is that the heat load to the walls in normal operation will be of the order of 10 MW/m² with excursions to 20 MW/m² during unstable plasma events such as ELMs (Edge Localized Modes). To put this in perspective, an arc welder delivers a heat load of about 40 MW/m² so clearly, such high heat loads expected during operation, can be very destructive to the plasma facing components of the reactor. These problems are most apparent in the divertor region into which plasma is scraped off from the main toroidal region (the pedestal). This allows helium “ash” to be removed from the burning plasma by pumping and the divertor is also one of the means of extracting energy from the reactor.

2. High Temperature Energy Loss Processes
In the divertor region, the plasma is cooler than in the central core and one can expect to find electrons with energy in the range (0.1-200 eV) at a density of ~ 10^{14} cm⁻³. In the core, where the thermonuclear reaction will take place, once the machine is fuelled with tritium and deuterium, the electron energies are in the range 0.2-20 keV. In earlier tokamaks such as the Princeton Large Torus (PLT), it was found that serious energy loss in the plasma could be attributed to the emission of photons due to dielectronic recombination:

\[ e + A^{z+} \rightarrow A^{(z-1)+} \rightarrow A^{(z-1)+} + h\nu \]
and electron impact excitation followed by radiative relaxation:
\[ e(E) + A^{z+} \rightarrow e(E') + A^{z+*} \rightarrow e(E') + A^{z+} + h\nu \]
of multiply charged ions of heavy metal impurities \((A^{z+})\), generated by the interaction of the plasma with the walls of the reactor. In these reactions in the tokamak, the ions are typically highly charged and thus the emitted photons are in the x-ray range and thus carry away a large amount of energy. The key point however, is that both of these collision processes require the ion target to contain electrons that can be excited. Following the realization of the significance of these reactions, carbon tiles were implemented as wall coverings and for plasma facing components and this allowed the energy of the plasmas in future machines (TFTR, JET, JT60) to be increased up to ignition conditions, for any carbon atom impurities entering the plasma, are rapidly fully ionized so that both dielectronic recombination and electron impact excitation loss processes are eliminated. The only recombination process that occurs is the radiative recombination reaction;
\[ e + C^{6+} \rightarrow C^{5+} + h\nu \]
that is at least two orders of magnitude slower that dielectronic recombination.

3. Wall Materials
While carbon has been the material of choice for the walls of most tokamaks up to the present, it does however, present different problems that have become apparent through usage. Firstly it is a reactive material and is rapidly eroded by interaction with the hydrogen plasma leading to the generation of hydrocarbon ions that serve as nuclei for the formation of carbon dust. This dust is electrostatically charged and can be carried along the magnetic field lines and be dumped elsewhere in the machine, in the divertor regions for example. This is a nuisance rather that a fatal flaw but the fact that when running in a thermonuclear mode, the hydrogen is replaced with radioactive tritium and this becomes bound up in the carbon tiles and the dust, this becomes a very serious problem both from fuel depletion and from safety points of view. Although carbon will be used for initial experiments, it will be eventually be replaced by beryllium as the plasma facing material on the walls of ITER.

4. Plasma Cooling
While the goal of tokamaks is to heat up, sustain and confine a plasma at very high temperature so as to allow isotopes of hydrogen to fuse together and produce energy, in the divertor and near the walls, one needs to cool down the plasma to avoid material damage to the components. In order to do this, impurities such a neon or argon are puffed into the divertor where the energy of the electrons is taken up in ionizing these gases which, becoming fully ionized, do not cause problems if they drift back into the central hot core region. Other elements that can perhaps be found in the divertor region are nitrogen and oxygen which may be due to issues connected with vacuum technology (leaks, outgassing of water, etc.). With the electron temperature being lower in the divertor region, the plasma is very different from that in the main core. Indeed molecules are formed due to recombination on surfaces and these ro-vibrationally excited species return to the plasma causing a very rich chemistry to be generated. Knowledge of this chemistry and in particular of the ion chemistry, is very important, for it is desirable that ions are neutralized prior to reaching the surfaces of the components so that the recombination energy is not released in the surface. Thus dissociative recombination plays an important role in this region and it is necessary to have good state-to-state knowledge of this process. Molecular ions can also be formed in the volume through three-body processes and by ion-molecule reactions. In this paper we shall discuss just the elements with atomic number 1 to 4 i.e. hydrogen, helium, lithium and beryllium. Lithium is included for it may be used for diagnostic processes. Since this paper covers a very wide range of subjects, with a few exceptions, we shall not give specific references to excited state distributions, reaction cross sections etc. The reader is directed towards the standard literature and previous proceedings of this conference for further information on these processes.
5. Light Element Chemistry

In this paper, for the light elements H, He, Li and Be, the most important species that are likely to be found in the divertor and at the plasma edge are given in Table I:

| Table I: Primary species |
|--------------------------|
| H⁺, He⁺, He+++ , Li⁺, Li++ , Be+++ dominant boundary species |
| H⁺, H, He, He*, H₂(v) |
| H₂⁺(v), H₂⁺(v), He₂⁺(v), HeH⁺(v), HeH++(v), LiH⁺(v), BeH⁺(v) |
| NeH⁺(v), ArH⁺(v), HeNe⁺(v) |

An important thing to note is that many of these species will be present in excited states. This is particularly true of H, He, He⁺ and HeH⁺, all of which have long lived electronically excited states and the molecular ions will initially be in ro-vibrationally excited states and this will greatly affect the reaction cross sections. As mentioned above, neon and argon will be present if deliberately introduced into the plasma for cooling purposes.

Information on the formation, reaction and destruction mechanisms for these species is crucial for accurate and complete models of the plasma chemistry in ITER. The International Atomic Energy Authority (IAEA) has begun a Collaborative Research Program (CRP) specifically dealing with small light elements and their reactions [2]. For hydrogen molecular ions, the following reactions listed in Table II must be taken into account. Of particular note is the need to understand the initial distribution of vibrational states of the hydrogen molecule formed on the surface, that for the hydrogen molecular ion created by electron impact and the subsequent life history of these distributions. State-to-state reaction cross sections therefore need to be known and evaluated as to their relative importance. Although the table deals mainly with electron impact processes, there will also be a strong photon flux in the divertor region and so photoionisation and photodissociation processes must also be taken account of. Possibly even photon stimulated processes may play a role although this has to be evaluated. For example almost nothing is known concerning the dissociative recombination of molecular ions in a strong radiation field. Given the uncertainties in this area, we shall consider that these are outside the scope of the present paper but nevertheless they should not be forgotten.

| Table II: Hydrogen molecular ion reactions |
|--------------------------------------------|
| H₂, H₂⁺, H₁⁺  |
| H + H → H₂(v).......................... Surface recombination |
| H⁺ + H + X → H₂⁺(v) + X..............3-body-process |
| H⁺ + H → H₂⁺(v) + e .................. Associative ionization |
| H₂ (v) + e → H₂⁺(v) + 2e.............. Ionization |
| H₂⁺(v) + e → H + H + e ............. Dissociation |
| H₂⁺(v) + e → H + H + e ................ DR |
| H₂⁺(v) + e → H + H⁺ + e............. DE |
| H₂⁺(v) + e → H⁺ + H⁺ + 2e.......... DI |
| H₂⁺(v) + H₁ → H₂⁺(v) + H...... Ion-Molecule |
| H₂⁺(v) + He → H₂⁺(v) + H... Ion-Molecule |
| H₂⁺(v) + Ne → NeH⁺ + H... Ion-Molecule |
| H₂⁺(v) + e → H + H + H........... DR |
| H₂⁺(v) + e → H₂ + H.................. DR |
| H₂⁺(v) + e → H₂⁺ + H............. Ion-pair |
| H₂⁺(v) + e → H₂⁺ + H + e.......... DE |
| H₂⁺(v) + e → H₂ + H⁺ + e......... DE |
Molecular hydrogen will primarily be formed by the recombination of hydrogen atoms on surfaces and this leads to the production of vibrationally excited hydrogen molecules. Thus when ionized by electron impact, the resulting hydrogen ions will have a distribution of vibrational states populated, that is different from that formed from ground state ions. These vibrational states for homonuclear hydrogen and hydrogen isotopomers (D\textsubscript{2}+, T\textsubscript{2}+) have extremely long lifetimes (~10\textsuperscript{6} s) against radiative decay. Vibrationally excited H\textsubscript{2}\textsuperscript{*} molecules can however, react with helium and neon through endothermic reactions (see below) and this could lead to a low vibrational state population for the surviving molecular ions. The reaction with argon is energy neutral and so this is not the case for the case of argon addition to the plasma. Heteronuclear isotopomers (HD\textsuperscript{*}, DT\textsuperscript{*}) will of course rapidly radiatively decay to their ground states.

While dissociative recombination is a reaction that is not only important but much desired in the divertor region, the high electron energies encountered will mean that in fact dissociative excitation may actually be dominant and dissociative ionisation must be included. This has been discussed in more detail in refs. [3,4].

Those of us who work with afterglow plasmas know well that He\textsubscript{2}\textsuperscript{*} (Table III) is an important ion that is efficiently formed by three-body processes even at quite low pressures. This ion has played a special role in the history of recombination research as discussed by Rainer Johnsen in these proceedings. Ion storage ring measurements have shown that while the ground state ion has an extremely low recombination cross section, that for excited He\textsubscript{2}\textsuperscript{*} ions is substantial. Here is a very good example of the need for information on excited state chemistry. There is also a peak in the DR cross section at higher electron energies, even for ground state ions, and the dissociative excitation cross section for ground state ions has been measured in a storage ring experiment [5]. Resonant dissociative excitation [6] plays a role here yielding measurable cross sections below the expected threshold for this reaction and this is a phenomenon that must be taken into account in theoretical studies of this process.

Table III: He\textsubscript{2}\textsuperscript{*} reactions

| Reaction |
|----------|
| He\textsubscript{2}\textsuperscript{*} |
| He\textsuperscript{*} + He + X → He\textsubscript{2}\textsuperscript{*} + X……..3-body-process |
| He\textsubscript{2}\textsuperscript{*}(v) + e → He + He………………..DR |
| He\textsubscript{2}\textsuperscript{*}(v) + e → He + He\textsuperscript{*} + e…………DE |
| He\textsubscript{2}\textsuperscript{*}(v) + e → He\textsuperscript{*} + He\textsuperscript{*} +2e………..DI |

HeH\textsuperscript{*} is an ion that is expected to be present, being formed as shown in table II although three-body processes may also play a role, given that atomic hydrogen is likely to be more abundant than H\textsubscript{2} in the divertor. The reactions listed in table IV will then lead to its demise. As constantly re-stated in this review, the need for information on the reactivity of excited states is paramount and this means that experiments should be designed that allow excited states of heteronuclear ions to be examined. Much of the interest in dissociative recombination research has been concerned with ground state ions, especially for interstellar chemistry applications. Indeed one of the main features of the storage ring technique is its ability to allow ions to radiatively cool before measurements are performed. In fact, this is somewhat of a disadvantage for the data needed here and it shows the need for single-pass type experiments where the excited state can be adjusted by ion source conditions. An
example of this is shown in figure 1, recalling merged beam measurements \[7\] of the recombination of HeH\(^{+}\) ions where the excited state of the ions was tuned by varying the extraction voltage of the ion trap source. As seen, the ions extracted at an elevated extraction voltage (100V) display a cross section about a factor of 4-5 times greater than those extracted at a low voltage where the ions were ro-vibrationally much cooler. The actual excited state energy (though probably not the state distribution) can be determined by means of dissociative excitation threshold measurements coupled with theoretical studies (though this is complicated by the resonance DE mechanism). Though inexact, this type of measurement at least gives an indication of the overall effect of internal excitation on the reaction cross sections.

**Table IV: HeH\(^{+}\) reactions**

| Reaction |
|----------|
| HeH\(^{+}\) + e → He\(^{+}\) + H + e ..........Dr |
| He\(^{+}\) + H + X → HeH + X ..........3-body-process |

**Table V: Lithium and beryllium reactions**

| Reaction |
|----------|
| LiH\(^{+}\) + e → Li + H ..........Dr |
| LiH\(^{+}\) + H ..........No reaction |

Reactions with neon and argon (Table VI) are important as they will efficiently remove H\(^{2+}\) ions from the plasma and the effect of neon on the vibrational state distribution has been noted above. Experiment \[12\] have shown that ArH\(^{+}\) does not recombine at low energies though excited ions might. This is because the channel leading to Ar + H(n=2) is endothermic and the likelihood of the ion recombining to ground state products is very low. The cross section for DR and DE does rise however at higher electron energies. Experiment has also shown that NeH\(^{+}\) recombines at low energy \[13\] though theoretical calculations appear to show that this is only possible for vibrationally excited ions. The storage ring measurements of NeH\(^{+}\) DR and DE were complemented by crossed beam studies of DE and DI \[15\].
Given that ArH⁺ formation will not create as much of a dis-equilibrium of the vibrational distribution of H₂⁺ in the plasma, perhaps this element is a more desirable choice for plasma cooling operation than neon but this must await real in-situ experiments in the ITER divertor.

Table VI: Neon and argon reactions

| Reaction                      |
|-------------------------------|
| NeH⁺                          |
| NeH⁺ + e → Ne + H             |
| NeH⁺ + H₂ → products          |
| ArH⁺                          |
| ArH⁺ + e ≠                    |
| ArH⁺ + H₂ → H₃⁺ + Ar          |

The final set of reactions that are highlighted here are those concerning ro-vibrational excitation-de-excitation as listed in Table VII. These have been discussed in previous proceedings of this conference [16]. What is very striking about these reactions is their very large cross sections and so these must of necessity be included in plasma chemistry models.

Table VII: Electron impact rovibrational excitation

| Reaction                      |
|-------------------------------|
| H₂⁺(v,J) + e → H₂⁺(v’,J’) + e |
| HeH⁺(v,J) + e → HeH⁺(v’,J’) + e|
| H₃⁺(v,J) + e → H₃⁺(v’,J’) + e  |
| He₂⁺(v,J) + e → He₂⁺(v’,J’) + e|
| LiH⁺(v,J) + e → LiH⁺(v’,J’) + e|
| BeH⁺(v,J) + e → BeH⁺(v’,J’) + e|
| NeH⁺(v,J) + e → NeH⁺(v’,J’) + e|
| ArH⁺(v,J) + e → ArH⁺(v’,J’) + e|
Fig. 1: Merged beam cross sections for the dissociative recombination of \( \text{HeH}^+ \) taken with high and low ion extraction voltages. The upper curve corresponds to metastable excited ions that displayed a dissociative excitation threshold of about 2 eV.

6. Conclusions

Much of the data needed for light element chemistry modelling in ITER already exists though predominantly for ground state species. There is a need to understand what role excited states will play and how the excited state distributions will evolve with time in the machine. Unlike other tokamaks, pulse lengths in ITER can be up to 100 s long so this is an important point to take into account in order to understand the temporal evolution of the plasma in the divertor and wall regions. Experimental access to this type of information must surely be limited so there is a great need for theoretical studies to compliment the existing data and to show how reaction cross sections will be affected by different internal ion states. Although not discussed in detail above, the role of negative ions must also be considered. H\(^-\) ions can be formed on surfaces [17] and can re-enter the plasma where they will react with positive species via ion-ion processes. This is an area that also needs further study. ITER is a very exciting project and its success will depend on the resolution of all the technical difficulties that it will encounter. Certainly atomic and molecular processes will play an important role and there is a great challenge for the community to continue to study these processes so that we might understand their relative importance in regulating the temperature of the plasma in the near wall and divertor regions.

Other light elements that should be considered in the modelling of the cooler plasma regions in ITER include carbon (the initial wall material), nitrogen (another gas used as a coolant) and oxygen (absorbed and adsorbed on surfaces during periods when the machine is let up to air). The chemistry of these elements will be discussed elsewhere.
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