Supporting Information

Ar chemistry

We follow the following types of particles: Ar neutral atoms in the ground state, *e* electrons, Ar^+ ions, Ar_2^+ molecular ions, and the excitation levels of 4s and 4p considered in the single lumped excitation levels: Ar(4s) and Ar(4p). The different collisions and radiative processes considered in the QN and PS models are presented in **Table SI.1** and **Table SI.2**.

Table SI.1. Electron-heavy particle collisions included in the QN and PS models.

Reaction	**E_{th} [eV]**	**Rate coefficient *k* [$m^3\ s^{-1}$]**[a)]	**Reference**
e + Ar → e + Ar , *elastic*	-	BOLSIG+[b)]	[1]
e + Ar → e + Ar(4s), *excitation*	11.55	BOLSIG+	[1]
e + Ar(4s) → e + Ar, *de-excitation*	-11.55	BOLSIG+, DB[c)]	[1]
e + Ar → 2e + Ar^+, *direct ionization*	15.7	BOLSIG+	[1]
e + Ar(4s) → 2e + Ar^+	4.15	BOLSIG+	[2]
e + Ar → e + Ar(4p), *excitation*	13	BOLSIG+	[1]
e + Ar(4p) → e + Ar, *de-excitation*	-13	BOLSIG+, DB	[1]
e + Ar(4p) → 2e + Ar^+	2.8	BOLSIG+	[2]
e + Ar(4s) → e + Ar(4p)	1.08	BOLSIG+	[3]
e + Ar(4p) → e + Ar(4s)	-1.08	BOLSIG+, DB	[3]
Ar^+ + 2e → Ar + e, *3-body recombination*	-	$8.75 \times 10^{-39}(T_e(eV))^{-4.5}$ [$m^6\ s^{-1}$]	[4]
Ar^+ + e + Ar → Ar + Ar	-	$1.5 \times 10^{-40}\left[\frac{300}{T_g(K)}\right]^{2.5}$ [$m^6\ s^{-1}$]	[5]
e + Ar_2^+ → Ar^+ + Ar + e, *electron impact*	-	$1.11 \times 10^{-12}\exp\left(-\frac{2.94-3(T_g(eV)-0.026)}{T_e(eV)}\right)$	[6]
e + Ar_2^+ → Ar + Ar(4s)	-	$1.04 \times 10^{-12}\left(\frac{300}{T_e(K)}\right)^{0.67}\frac{1-\exp[-418/T_g(K)]}{1-0.31\exp[-418/T_g(K)]}$	[7, 8]

[a] The rate coefficient for 3-body collisions has unit [m^6 s^{-1}] and is explicitly mentioned where applicable; [b] Boltzmann solver: the rate coefficients are calculated from the corresponding cross sections, based on solution of the Boltzmann equation with BOLSIG+[9]; [c] Detailed balance (DB): the rate coefficients for the superelastic processes are calculated using the detailed balance principle[10] incorporated in BOLSIG+[9].

Table SI.2. Heavy particle-heavy particle collisions and radiative transitions included in the QN and PS models.

Reaction	**Rate coefficient k [m^3 s^{-1}] / collision frequency ν_c [s^{-1}]**	**Reference**
Ar(4s) + Ar(4s) → Ar_2^+ + e	$k = \frac{1}{2} 6.3 \times 10^{-16} \left[\frac{300}{T_g(K)}\right]^{1/2}$	[11]
Ar(4s) + Ar(4s) → Ar^+ + Ar + e	$k = 6.2 \times 10^{-16}$	[12]
Ar^+ + 2Ar → Ar_2^+ + Ar	$k = 2.5 \times 10^{-43} \left(\frac{300}{T_g(K)}\right)^{3/2}$ [m^6 s^{-1}]	[13]
Ar_2^+ + Ar → Ar^+ + 2Ar	$k = \frac{6.06 \times 10^{-12}}{T_g(K)} exp\left(-\frac{1.51 \times 10^4}{T_g(K)}\right)$	[6]
Ar(4p) + Ar → Ar(4s) + Ar	$k = 5 \times 10^{-18}$	[13]
Ar(4s) + Ar(4p) → Ar^+ + Ar + e	$k = 6.2 \times 10^{-16}$	[12]
Ar(4p) + Ar(4p) → Ar^+ + Ar + e	$k = 6.2 \times 10^{-16}$	[12]
Ar(4s) → Ar + $h\nu$	$\nu_c = {g_{eff}}^{b)} \times 3.145 \times 10^8$	[14]
Ar(4p) → Ar(4s) + $h\nu$	$\nu_c = 4.4 \times 10^8$	[14]

[a] The rate coefficient for 3-body collisions has unit [m^6 s^{-1}] and is explicitly mentioned where applicable; [b] g_{eff} depends on the characteristic dimension of the reactor and is calculated to be 6×10^4 for the present reactor.[15]

In the QN model, the reaction rates for the Ar^+-Ar elastic isotropic scattering and scattering in backward direction (to simulate charge transfer) are calculated based on the momentum transfer

cross-sections.[16] In the PS model these rates are included in the calculation of the Ar^+ ion diffusion and mobility coefficients.[17]

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