

Plasma and Dry Micro/Nanotechnologies

3. Chemical and Plasma Kinetics

Lenka Zajíčková

Faculty of Science, Masaryk University, Brno &
Central European Institute of Technology - CEITEC

lenkaz@physics.muni.cz

spring semester 2023



Central European Institute of Technology
BRNO | CZECH REPUBLIC



● 3. Chemical and Plasma Kinetics

3.1 Chemical Kinetics

3.2 Plasma Kinetics

3.3 Elementary Processes in Plasma Involving Atoms

3.4 Elementary Processes in Plasma Involving Molecules

Chemical vapor deposition (CVD): based on chemical reactions.

Plasmachemical processing of materials (plasma treatment in reactive gases, plasma etching, plasma enhanced CVD - PECVD): chemical reactions with reactive species activated by hot electrons.

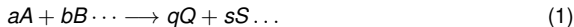
- ▶ **homogeneous** - if reactants are of the same phase (e.g. reactions in gas phase)
- ▶ **heterogeneous** - if reactants are of two or more different phases (e.g. reaction between gas and solid - deposition, etching)

Related terms:

- ▶ reaction rate, reaction order, rate constant, Arrhenius plot
- ▶ elastic collisions (Coulomb, polarization scattering with permanent or induced dipole, hard sphere scattering)
- ▶ inelastic collisions (ionization, recombination, excitation, dissociation ...)
- ▶ collisional cross-section and its relation to the reaction constant

3.1 Chemical Kinetics

Consider the reaction



The reactants A and B react with the rate

$$r'_A = -\frac{dN_A}{dt} \quad r'_B = -\frac{dN_B}{dt}. \quad (2)$$

The products Q and S are created with the rate

$$r'_S = \frac{dN_S}{dt} \quad r'_Q = \frac{dN_Q}{dt}, \quad (3)$$

where N_j is molar amount (usually in kmol) and t is time.

$$r' = -\frac{1}{a} \frac{dN_A}{dt} = -\frac{1}{b} \frac{dN_B}{dt} = \frac{1}{q} \frac{dN_Q}{dt} = \frac{1}{s} \frac{dN_S}{dt}. \quad (4)$$

The **reaction rate** is generally expressed on an intensive basis, e.g. reaction volume V .

$$r = \frac{-1}{aV} \frac{dN_A}{dt} = \frac{-1}{aV} \frac{d}{dt}(C_A V) = \frac{-1}{aV} \left(V \frac{dC_A}{dt} + C_A \frac{dV}{dt} \right), \quad (5)$$

where C_A is the molar concentration of A (kmol/m³). When the volume is constant

$$r = \frac{-1}{a} \frac{dC_A}{dt}. \quad (6)$$

3.1 Chemical Kinetics

The **reaction rate** can be expressed also as

$$r = k_{AB} C_A^a C_B^b. \quad (7)$$

where k_{AB} is the **rate constant** of the reaction $aA + bB \rightarrow$ products.

- ▶ The powers a, b are called **partial orders** of the reactions.
- ▶ The sum $a + b$ is (global) **order**.

The partial orders should be in fact replaced by a', b' determined experimentally because they coincide with the stoichiometric coefficients only for elementary processes.

Arrhenius concluded from thermodynamics (T is temperature, R and k_B gas and Boltzmann constants):

$$\ln k = -\frac{\varepsilon_a}{RT} + \ln A_0 = -\frac{E_a}{k_B T} + \ln A_0$$

ε_a and E_a **activation energies** in J/mol and J, A_0 constant frequency factor.

3.1 Chemical Kinetics

For **non-reversible first order reaction** $A \rightarrow Q$, we have at constant volume

$$r = -\frac{dC_A}{dt} = kC_A. \quad (8)$$

If we know the rate constant k (hr^{-1}), we can calculate the reaction rate r for any concentration of the reactant.

The rate constant k can be calculated from Eq. (8) if we know the time change of the concentration \Rightarrow differential method. **Integral method** uses integrated Eq. (8):

$$\ln\left(\frac{C_{A0}}{C_A}\right) = kt. \quad (9)$$

The semilog plot of C_{A0}/C_A in dependence on time gives k .

Now, think about the expressions for

- ▶ reversible 1st order reaction $A \xrightleftharpoons[2]{1} Q$
- ▶ irreversible 2nd order reaction $2A \rightarrow Q + S$
- ▶ irreversible 2nd order reaction $A + B \rightarrow Q + S$

We can encounter also with **complex reactions**: parallel, consecutive, free radical chain reaction (initiation, propagation, termination), free radical addition

3.2 Plasma Kinetics

Elastic collisions (momentum and energy are conserved):

- ▶ **Coulomb** collisions - between two charged particles (e-e, e-ion, ion-ion)
- ▶ polarization scattering with **permanent dipole** (for molecules with permanent dipole)
- ▶ polarization scattering with **induced dipole** (e-neutral for electrons with low energies, ion-neutral collisions)
- ▶ **hard sphere** - between neutrals, e-neutral for very low electron energies (approx.)

TABLE 3.1. Scaling of Cross Section σ , Interaction Frequency ν , and Rate Constant K , With Relative Velocity v_R , for Various Scattering Potentials U

| Process | $U(r)$ | σ | ν or K |
|------------------|-------------------------------|-----------|--------------|
| Coulomb | $1/r$ | $1/v_R^4$ | $1/v_R^3$ |
| Permanent dipole | $1/r^2$ | $1/v_R^2$ | $1/v_R$ |
| Induced dipole | $1/r^4$ | $1/v_R$ | const |
| Hard sphere | $1/r^i, i \rightarrow \infty$ | const | v_R |

after Lieberman & Lichtenberg 1994

Inelastic collisions: ionization, recombination, excitation, dissociation . . .

3.2 Plasma Kinetics

Electrons in plasma gain high energies (in the order of 1–10 eV) due to acceleration by electric field.

Since electrons collide with heavy particles (atoms, molecules) they change direction of their velocity or even lose the energy.

Collisions between electrons and heavy particles (according to the electron energy E_e):

- ▶ $E_e < 2 \text{ eV}$ (depending on the atom/molecule): elastic collisions with very small fractional energy transfer (see slide in Atomic Collisions).
- ▶ $2 \text{ eV} < E_e < 15 \text{ eV}$ (approx.): variety of inelastic collisions $\Rightarrow E_e$ is partially converted into internal energy of the target molecule (atom)
- ▶ $E_e > 15 \text{ eV}$ (approx.): ionization (sustains the discharge)

Rate constant k for reaction of two particles with velocities \vec{v}_1, \vec{v}_2 can be calculated from **cross section** σ

$$k = \langle \sigma(v_R) v_R \rangle_{v_1, v_2} = \int \sigma(v_R) v_R f_1(\vec{v}_1) f_2(\vec{v}_2) dv_1^3 dv_2^3$$

where $v_R = |\vec{v}_1 - \vec{v}_2|$ and $f_1(\vec{v}_1), f_2(\vec{v}_2)$ are velocity distribution functions.

Plasma Kinetics

The velocity distributions are taken **isotropic Maxwellian**.

$$f(\mathbf{v}) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{m\mathbf{v}^2}{2k_B T} \right)$$

where m and T are particle mass and temperature.

If the characteristics velocities of target particles are much less than those of incident particles (e. g. electron collision with heavy particle) $v_R \approx |\vec{v}_1| \equiv v$.

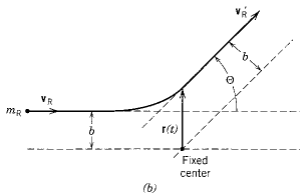
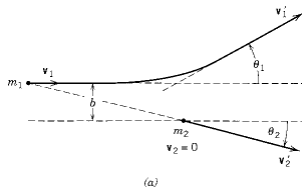
$$k(T) = \langle \sigma(v)v \rangle_v = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty \sigma(v)v \exp \left(-\frac{mv^2}{2k_B T} \right) 4\pi v^2 dv$$

If we consider collision of two different heavy particles

$$k(T) = \langle \sigma(v_R)v_R \rangle_{v_1, v_2} = \left(\frac{m_R}{2\pi k_B T} \right)^{3/2} \int_0^\infty \sigma(v_R)v_R \exp \left(-\frac{mv_R^2}{2k_B T} \right) 4\pi v_R^2 dv_R$$

where m_R is reduce mass.

3.3 Atomic Collisions / Elastic scattering



Scattering in (a) laboratory system, (b) the center of mass (CM) system (after Lieberman & Lichtenberg 1994).

Electron - atom elastic collision:

- ▶ momentum and energy are conserved,
- ▶ treated as hard-sphere scattering

Fraction of energy lost by the projectile in the laboratory system

$$\gamma = \frac{E_t}{E_i} = \frac{4m_1 m_2}{(m_1 + m_2)^2} \cos^2 \theta_2$$

and in the CM system

$$\gamma = \frac{E_t}{E_i} = \frac{2m_1 m_2}{(m_1 + m_2)^2} (1 - \cos \Theta)$$

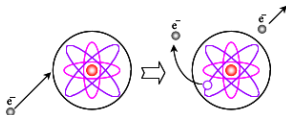
Average loss obtained by averaging over all angles Θ using differential cross section $\sigma(v_R, \Theta)$ as distribution function

$$\langle \gamma \rangle_{\Theta} = \frac{2m_1 m_2}{(m_1 + m_2)^2} \frac{\int_0^{\pi} (1 - \cos \Theta) \sigma(v_R) 2\pi \sin \Theta d\Theta}{\int_0^{\pi} \sigma(v_R) 2\pi \sin \Theta d\Theta}$$

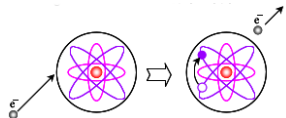
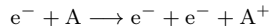
for $m_1 = m_e$, $m_2 = M$ and $m_e \ll M$

$$\langle \gamma \rangle_{\Theta} = \frac{2m_1 m_2}{(m_1 + m_2)^2} \approx \frac{2m_e}{M} \approx 10^{-4}$$

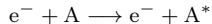
3.3 Atomic Processes / Excitation Processes



Electron impact ionization

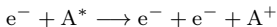


Electron impact excitation



A^* can have quite different chemical reactivity towards the surface. Some excited atoms have very long lifetimes ($\approx 1-10$ ms) \Rightarrow **metastables**

Electron-metastable ionization

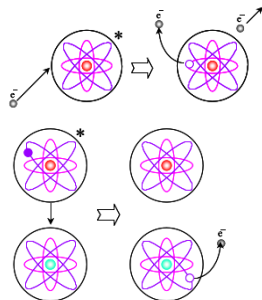


Since the metastable atom is already excited, less energy is required.

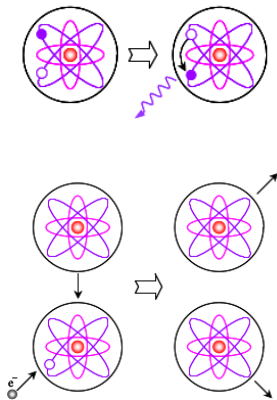
Metastable-neutral ionization



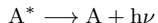
If the ionization energy of the neutral B is less than the excitation energy of the metastable $A^* \Rightarrow$ **Penning ionization** (He* 19.8, Ne* 16.7, Ar* 11.7 eV)



Atomic Processes - Relaxation and Recombination

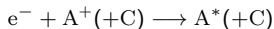


De-excitation



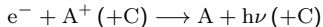
In most cases, the relaxation of electronically excited states is practically instantaneous (≈ 10 ns).

Electron-ion recombination

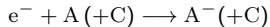


A third-body (neutrals, reactor walls) must be involved to conserve energy and momentum.

Radiative recombination



Electron attachment



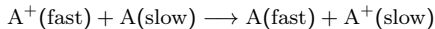
Ion-ion recombination



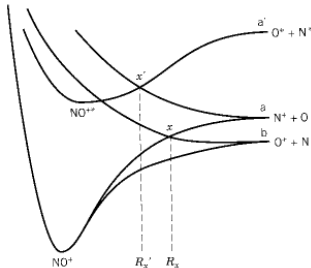
Heavy-Particle Collisions - Charge Transfer

- ▶ In general, the energy level from which e^- is released is not equal to the energy level into which the electron is captured \Rightarrow energy defect ΔW .
- ▶ For $\Delta W \neq 0$, the kinetic energy of the colliding particles is not conserved in the collision.

Resonant charge transfer If atom and ion are parent and child, the transfer occur with $\Delta W = 0$



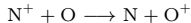
Cross section is larger for low energies, important process in weakly ionized plasmas.



Nonresonant charge transfer



Illustrated for $N^+ + O$ and $O^+ + N$ (ioniz. potential of N and O are 14.53 and 13.61 eV, respectively)
Exothermic reaction a-x-b



does not have a threshold energy, products share an increased kinetic energy of 0.92 eV.

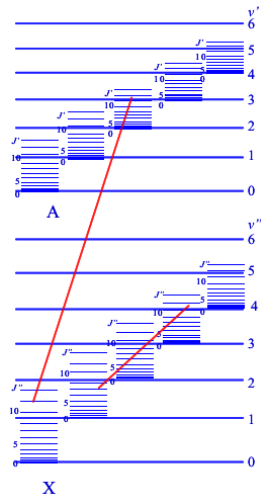
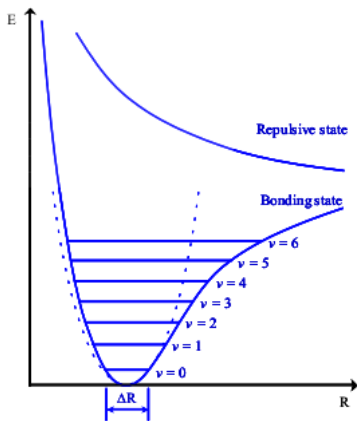
The inverse endothermic reaction ($\varepsilon_{\text{thr}} = 0.92$ eV) has very small rate constant at thermal energies



but if O^+ or N are excited, the reaction $a'-x'-a$ has no ε_{thr} and σ can be large at thermal energies.

3.4 Elementary Processes in Plasma Involving Molecules

In molecules, **excitation of vibrational and rotational states** (besides electronic states) are possible:



Electron Collisions with Molecules - Interaction Times

Interaction times:

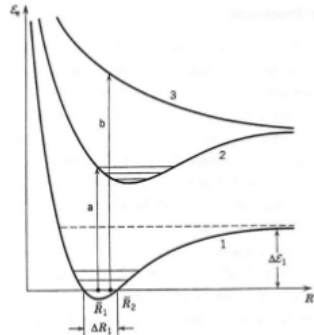
- ▶ electron motion in the molecule $t_{\text{at}} \approx 10^{-16}\text{--}10^{-15}$ s
- ▶ interaction time of e^- with molecule $t_{\text{int}} \approx 10^{-16}\text{--}10^{-15}$ s
- ▶ typical vibrational period of molecule $t_{\text{vib}} \approx 10^{-14}\text{--}10^{-13}$ s
- ▶ typical time for molecule dissociation $t_{\text{diss}} \approx 10^{-14}\text{--}10^{-13}$ s
- ▶ typical transition time for electric dipole radiation $t_{\text{rad}} \approx 10^{-9}\text{--}10^{-8}$ s
- ▶ typical time between e-molecule collisions in a low pressure plasma $t_{\text{col}} \approx 10^{-8}\text{--}10^{-6}$ s

$$t_{\text{at}} \sim t_{\text{int}} \ll t_{\text{vib}} \sim t_{\text{diss}} \ll t_{\text{rad}} < t_{\text{col}}$$

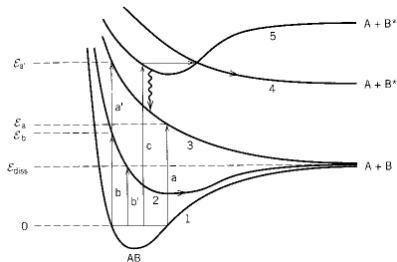
For electron collisional excitation of molecule to an excited electronic state, the new vibrational (and rotational) state can be determined by freezing the nuclear motion during the collision

$t_{\text{int}} \ll t_{\text{vib}} \sim t_{\text{diss}} \Rightarrow$ **Frank-Condon principle**

Since $t_{\text{diss}} \ll t_{\text{rad}}$, if energetics permit, the molecule will dissociate instead of de-exciting.



Electron Collisions with Molecules - Dissociation



Dissociation cross section rises linearly from threshold $\varepsilon_{\text{thr}} \approx \varepsilon_1$ to a max. value (typically 10^{-15} cm^2) at ε_2 and then falls off as $1/\varepsilon$:

$$\sigma_{\text{diss}} = 0 \quad \varepsilon < \varepsilon_1$$

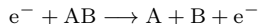
$$\sigma_{\text{diss}} = \sigma_0 \frac{\varepsilon - \varepsilon_1}{\varepsilon_1} \quad \varepsilon_1 < \varepsilon < \varepsilon_2$$

$$\sigma_{\text{diss}} = \sigma_0 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon} \quad \varepsilon > \varepsilon_2$$

$$\sigma_0 = \pi \left(\frac{e}{4\pi\epsilon_0\varepsilon_1} \right)^2$$

Dissociation

key role for plasma chemistry of low pressure discharges:



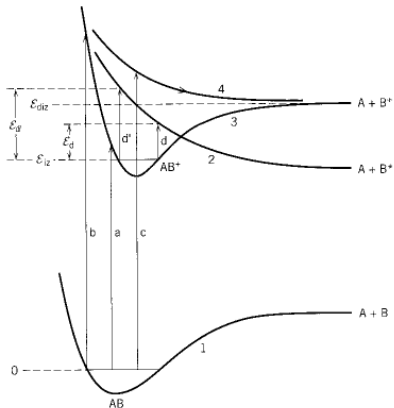
Collisions a and a': ground state $v = 0$ excited to repulsive state of AB, energy $\langle \varepsilon_a - \varepsilon_{\text{diss}}, \varepsilon_{a'} - \varepsilon_{\text{diss}} \rangle$ shared among the dissociation products A and B.

Typically, $\varepsilon_a - \varepsilon_{\text{diss}} \approx \text{few eV}$
 \Rightarrow **hot neutral fragments** (profound effect on plasma chemistry of growing films if hitting the substrate surface)

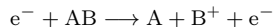
Collisions b and b': ground state excited to an attractive state of AB but energy exceeds $\varepsilon_{\text{diss}} \Rightarrow$ dissociation of AB resulting in fragments having energies from thermal up to $\varepsilon_b - \varepsilon_{\text{diss}} \approx \text{few eV}$.

Collision c: excitation to bound state AB* that radiates creating A + B or
 $AB^*(\text{bound}) \rightarrow AB^*(\text{unbound}) \rightarrow A+B^*$

Electron Collisions with Molecules - contin.

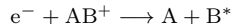


Dissociative Ionization (in addition to normal ionization)



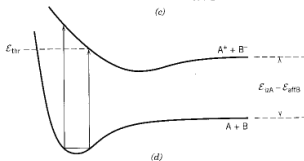
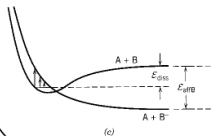
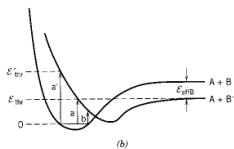
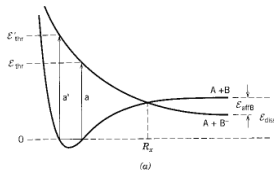
is common for polyatomic molecules. Formation of molecular ion (collision *a*) for threshold energy ϵ_{iz} . Collisions *b*, *c* for higher threshold energies $\epsilon_{diz} \Rightarrow$ fast ion and neutral.

Dissociative Recombination



collisions *d*, *d'* \Rightarrow fast excited neutral fragments.

Electron Collisions with Molecules - contin.



Dissociative Electron Attachment



important in discharges containing atoms with positive electron affinities because of

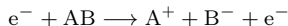
- ▶ production of negative ions
- ▶ threshold energy for dissociation is generally lower than for pure dissociation processes

(a) e^- capture into repulsive state \Rightarrow autodetachment or dissociation; autodetach. rate $\sqrt{M_R/m} \approx 100 \times$ dissociation rate (M_R reduced mass); hot fragments

(b) AB^- bound state $\Rightarrow a, a'$ dissociative attach. with low energy fragments; b collision $AB^{-*} \rightarrow e^- + AB$

(c) for few molecules (e.g. halogens) $\epsilon_{\text{affB}} > \epsilon_{\text{diss}} \Rightarrow$ slow e^- produce hot $A + B^-$; max. σ as high as 10^{-16} cm^2

Polar Dissociation (d)



- ▶ Maximum cross section and its dependence on electron impact energy are similar to pure dissociation.
- ▶ Threshold energy is generally large.

Electron Collisions with Molecules - contin.

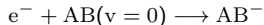
Electron Impact Detachment



similar to electron-neutral ionization with el. affinity ε_{aff} of AB playing the role of the ionization potential BUT the peak in cross section is shifted to energies of $10\text{--}20\varepsilon_{\text{aff}}$ due to repulsive Coulomb force between e^- and AB^- .

Vibrational and Rotational Excitations

Typically it is a two step process:



Life time of AB^- is $10^{-15}\text{--}10^{-10}$ s,

i. e. comparable or larger than its vibrational timescale 10^{-14} s \Rightarrow



Complex reaction schemes for O₂ plasma - 2nd order reactions

| Number | Reaction | Rate Constant (cm ³ /s) |
|--|--|---|
| <i>Reactions among e, O₂, O₂⁺, O, and O⁻</i> | | |
| 1 | e + O ₂ momentum transfer | 4.7E-8T _e ^{0.5} |
| 2 | e + O ₂ → O ⁻ + O | 1.07E-9T _e ^{-1.391} exp(-6.26/T _e) |
| 3 | e + O ₂ → 2O + e | 6.86E-9 exp(-6.29/T _e) |
| 4 | e + O ₂ → O ₂ ⁺ + 2e | 2.34E-9T _e ^{0.03} exp(-12.29/T _e) |
| 5 | e + O ⁻ → O + 2e | 5.47E-8T _e ^{0.324} exp(-2.98/T _e) |
| 6 | e + O ₂ ⁺ → 2O | 2.2E-8T _e ^{-0.72} |
| 7 | O ⁻ + O ₂ ⁺ → O + O ₂ | 2.6E-8(300/T) ^{0.44} |
| 8 | O ⁻ + O → O ₂ + e | (1.9, 3, 5)E-10 |
| 9 | O ⁻ + O ₂ ⁺ → 3O | 2.6E-8(300/T) ^{0.44} |
| <i>Addition of O⁺</i> | | |
| 10 | e + O ₂ → O ⁻ + O ⁺ + e | 7.1E-11T _e ^{0.5} exp(-17/T _e) |
| 11 | e + O ₂ → O + O ⁺ + 2e | 1.88E-10T _e ^{1.699} exp(-16.81/T _e) |
| 12 | e + O → O ⁺ + 2e | 9.0E-9T _e ^{0.7} exp(-13.6/T _e) |
| 13 | O ⁻ + O ⁺ → 2O | 4.0E-8(300/T) ^{0.44} |
| 14 | O ⁺ + O ₂ → O + O ₂ ⁺ | 2.0E-11(300/T) ^{0.5} |
| <i>Addition of metastable O₂⁺(¹Δ_g); see note f below</i> | | |
| 15 | e + O ₂ → O ₂ ⁺ + e | 1.37E-9 exp(-2.14/T _e) |
| 16 | e + O ₂ ⁺ → e + O ₂ | 2.06E-9 exp(-1.163/T _e) |
| 17 | e + O ₂ ⁺ → O + O ⁻ | 4.19E-9T _e ^{-1.376} exp(-5.19/T _e) |
| 18 | O ₂ ⁺ + O ₂ → 2O ₂ | 2.2E-18(7300) ^{0.8} |
| 19 | O ₂ ⁺ + O → O ₂ + O | (1.0, 7)E-16 |
| 20 | O ⁻ + O ₂ ⁺ → O ₃ + e | 2.2E-11 |
| 21 | O ⁻ + O ₂ ⁺ → O ₂ ⁻ + O | 1.1E-11 |
| <i>Addition of metastable O(¹D)</i> | | |
| 22 | e + O ₂ → O + O ⁺ + e | 3.49E-8 exp(-5.92/T _e) |
| 23 | e + O → O ⁺ + e | 4.54E-9 exp(-2.36/T _e) |
| 24 | e + O ⁺ → e + O | 8.17E-9 exp(-0.4/T _e) |
| 25 | e + O ⁺ → O ⁺ + 2e | 9.0E-9T _e ^{0.7} exp(-11.6/T _e) |
| 26 | O ⁺ + O → 2O | 8.0E-12 |
| 27 | O ⁺ + O ₂ → O + O ₂ | (6.4, 7.0)E-12 exp(67/T) |
| 28 | O ⁺ + O ₂ → O + O ₂ ⁺ | 1.0E-12 |
| <i>Addition of selected reactions for O₂⁻ and O₃</i> | | |
| 29 | O ⁻ + O ₂ → O ₃ + e | 5E-15 |
| 30 | e + O ₃ → O ₂ ⁻ + O | 1E-9 |
| 31 | e + O ₃ → O ⁻ + O ₂ | 2.12E-9T _e ^{-1.058} exp(-0.93/T _e) |
| 32 | O ₂ ⁻ + O ₂ ⁺ → 2O ₂ | 2E-7(300/T) ^{0.5} |
| 33 | O ₂ ⁻ + O ⁺ → O ₂ + O | (1, 2)E-7(300/T) ^{0.5} |
| 34 | O ₃ + O ₂ → O ₂ + O + O ₂ | 7.3E-10 exp(-11400/T) |
| 35 | O ₃ + O → 2O ₂ | 1.8E-11 exp(-2300/T) |

Complex reaction schemes for O₂ plasma - 3rd order reactions

| Number | Reaction | Rate Constant (cm ⁶ /s) |
|---|---|--|
| <i>Reactions among e, O₂, O₂⁺, and O⁻</i> | | |
| 1 | $e + e + O_2^+ \rightarrow e + O_2$ | $1E-19(0.026/T_e)^{4.5}$ |
| 2 | $e + O_2^+ + O_2 \rightarrow O_2 + O_2$ | $6E-27(0.026/T_e)^{1.5}, 1E-26$ |
| 3 | $e + O + O_2 \rightarrow O^- + O_2$ | $1E-31$ |
| 4 | $O^- + O_2^+ + O_2 \rightarrow O + O_2 + O_2$ | $2E-25(300/T)^{2.5}$ |
| 5 | $O + O + O_2 \rightarrow O_2 + O_2$ | $2.45E-31T^{-0.63}$ $1.3E-32(300/T)\exp(-170/T)$ |
| 6 | $O + O + O \rightarrow O_2 + O$ | $6.2E-32\exp(-750/T)$ |
| <i>Addition of O⁺</i> | | |
| 7 | $e + e + O^+ \rightarrow e + O$ | $1E-19(0.026/T_e)^{4.5}$ |
| 8 | $e + O^+ + O_2 \rightarrow O + O_2$ | $6E-27(0.026/T_e)^{1.5}, 1E-26$ |
| 9 | $O^- + O^+ + O_2 \rightarrow O_2 + O_2$ | $2E-25(300/T)^{2.5}, 2E-25$ |
| 10 | $O^- + O^+ + M \rightarrow O + O + M$ | $2E-25(300/T)^{2.5}$ |
| 11 | $O^+ + O + O_2 \rightarrow O_2^+ + O_2$ | $1E-29$ |
| <i>Addition of metastable O(¹D)</i> | | |
| 12 | $O + O^* + O_2 \rightarrow O_2 + O_2$ | $9.9E-33$ |
| <i>Addition of selected reactions for metastable O₂(¹Δ_g), O₂⁻, and O₃</i> | | |
| 13 | $e + O_2 + O_2 \rightarrow O_2^- + O_2$ | $1.4E-29(0.026/T_e)$ $\times \exp(100/T - 0.061/T_e)$ |
| 14 | $e + O_2 + O \rightarrow O_2^- + O$ | $1E-31$ |
| 15 | $O^- + O_2^+ + O_2 \rightarrow O_3 + O_2$ | $2E-25(300/T)^{2.5}$ |
| 16 | $O + O_2 + O_2 \rightarrow O_3 + O_2$ | $6.9E-34(300/T)^{1.25},$ $6.4E-35 \exp(663/T)$ |
| 17 | $O + O_2 + O \rightarrow O_3 + O$ | $2.15E-34 \exp(345/T)$ |
| 18 | $e + O_2^* + O_2 \rightarrow O_2^- + O_2$ | $1.9E-30$ |
| 19 | $e + O_2^* + O \rightarrow O_2^- + O$ | $1E-31$ |
| 20 | $O_2^- + O^+ + M \rightarrow O_3 + M$ | $2E-25(300/T)^{2.5}$ |
| 21 | $O_2^- + O_2^+ + O_2 \rightarrow O_2 + O_2 + O_2$ | $2E-25(300/T)^{2.5}$ |