

# F4280 Technologie depozice tenkých vrstev a povrchových úprav

## 7.2 Plasma Kinetics and Plasma Chemistry

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# 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 loose the energy.

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

- ▶  $E_e < 2$  eV (depending on the atom/molecule): elastic collisions with very small fractional energy transfer (see next slide).
- ▶  $2$  eV  $< E_e < 15$  eV (approx.): variety of inelastic collisions  $\Rightarrow E_e$  is partially converted into internal energy of the target molecule (atom)
- ▶  $E_e > 15$  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**  $\sigma$

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

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**.

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

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.

# Elastic Scattering

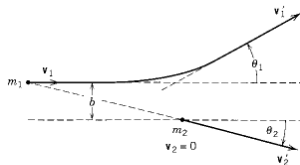
- ▶ Coulomb collisions - between two charged particles (e-e, e-ion, ion-ion)
- ▶ hard sphere - for neutrals, approx. for e-neutral for very low electron energies
- ▶ polarization scattering with induced dipole (e-neutral for electrons with low energies, ion-neutral)
- ▶ polarization scattering with permanent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

**TABLE 3.1. Scaling of Cross Section  $\sigma$ , Interaction Frequency  $\nu$ , and Rate Constant  $K$ , With Relative Velocity  $v_R$ , for Various Scattering Potentials  $U$**

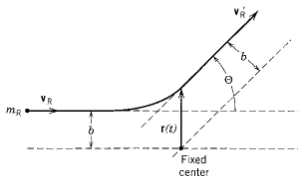
Process	$U(r)$	$\sigma$	$\nu$ or $K$
Coulomb	$1/r$	$1/v_R^4$	$1/v_R^3$
Permanent dipole	$1/r^2$	$1/v_R^2$	$1/v_R$
Induced dipole	$1/r^4$	$1/v_R$	const
Hard sphere	$1/r^i, i \rightarrow \infty$	const	$v_R$

after Lieberman & Lichtenberg 1994

# Atomic Collisions



(a)



(b)

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

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

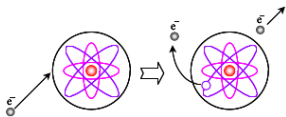
Average loss obtained by averaging over all angles  $\Theta$  using differential cross section  $\sigma(v_R, \Theta)$  as distribution function

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

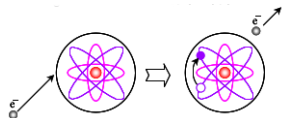
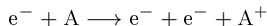
for  $m_1 = m_e$ ,  $m_2 = M$  and  $m_e \ll M$

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

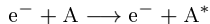
# Excitation Processes



## Electron impact ionization

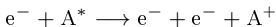


## Electron impact excitation



$A^{*}$  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

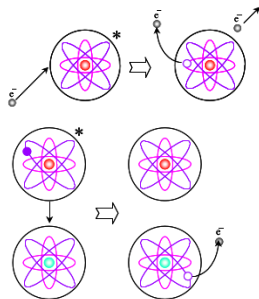


Since the metastable atom is already excited, less energy is required.

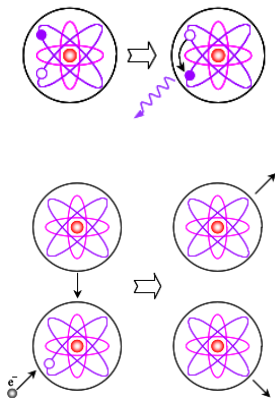
## Metastable-neutral ionization



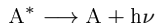
If the ionization energy of the neutral B is less than the excitation energy of the metastable  $A^{*} \Rightarrow$  **Penning ionization** (He\* 19.8, Ne\* 16.7, Ar\* 11.7 eV)



# Relaxation and Recombination Processes

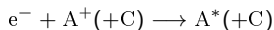


## De-excitation



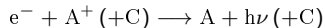
In most cases, the relaxation of electronically excited states is practically instantaneous ( $\approx 10$  ns).

## Electron-ion recombination

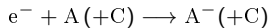


A third-body (neutrals, reactor walls) must be involved to conserve energy and momentum.

## Radiative recombination



## Electron attachment

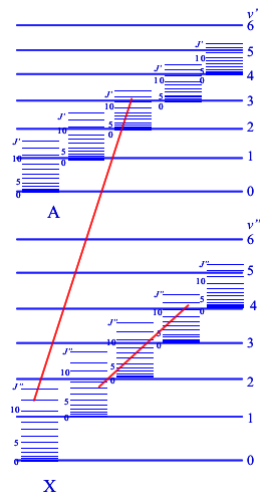
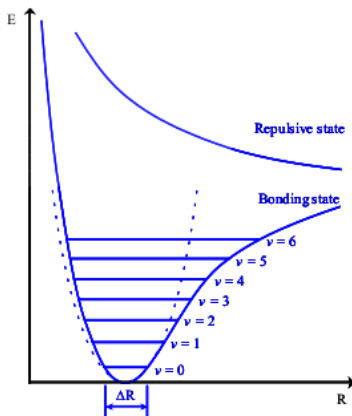


## Ion-ion recombination



# Molecular Collisions

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





# Electron collisions with molecules I

Interaction times:

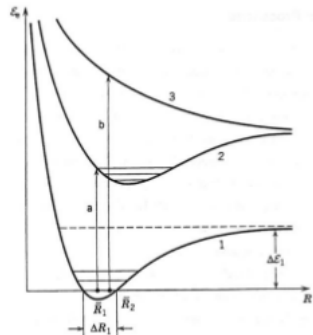
- ▶ electron motion in the molecule  $t_{\text{at}} \approx 10^{-16}\text{--}10^{-15}$  s
- ▶ interaction time of  $e^-$  with molecule  $t_{\text{int}} \approx 10^{-16}\text{--}10^{-15}$  s
- ▶ typical vibrational period of molecule  $t_{\text{vib}} \approx 10^{-14}\text{--}10^{-13}$  s
- ▶ typical 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

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

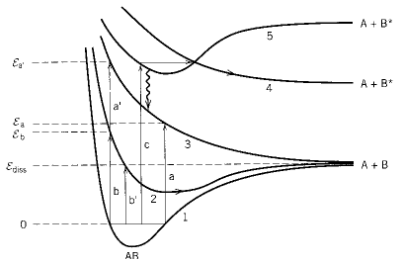
For electron collisional excitation of molecule to an excited electronic state, the new vibrational (and rotational) state can be determined by freezing the nuclear motion during the collision

$t_{\text{int}} \ll t_{\text{vib}} \sim t_{\text{diss}} \Rightarrow$  **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 II - Dissociation



Dissociation cross section rises linearly from threshold  $\varepsilon_{\text{thr}} \approx \varepsilon_1$  to a max. value (typically  $10^{-15} \text{ cm}^2$ ) at  $\varepsilon_2$  and then falls off as  $1/\varepsilon$ :

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

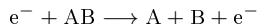
$$\sigma_{\text{diss}} = \sigma_0 \frac{\varepsilon - \varepsilon_1}{\varepsilon_1} \quad \varepsilon_1 < \varepsilon < \varepsilon_2$$

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

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

### Dissociation

key role for plasma chemistry of low pressure discharges:

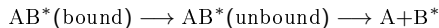


**Collisions a and a'**: ground state  $v = 0$  excited to repulsive state of AB, energy  $\langle \varepsilon_a - \varepsilon_{\text{diss}}, \varepsilon_{a'} - \varepsilon_{\text{diss}} \rangle$  shared among the dissociation products A and B.

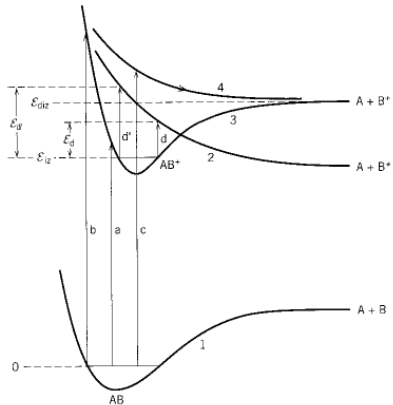
Typically,  $\varepsilon_a - \varepsilon_{\text{diss}} \approx \text{few eV}$   
 $\Rightarrow$  **hot neutral fragments** (profound effect on plasma chemistry of growing films if hitting the substrate surface)

**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  $\varepsilon_b - \varepsilon_{\text{diss}} \approx \text{few eV}$ .

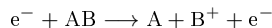
**Collision c**: excitation to bound state AB\* that radiates creating A + B or



## Electron collisions with molecules III

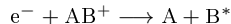


**Dissociative Ionization** (in addition to normal ionization)



is common for polyatomic molecules. Formation of molecular ion (collision *a*) for threshold energy  $\epsilon_{iz}$ . 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 IV

## Dissociative Electron Attachment



important in discharges containing atoms with positive electron affinities because of

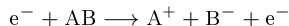
- ▶ production of negative ions
- ▶ threshold energy for dissociation is generally lower than for pure dissociation processes

(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

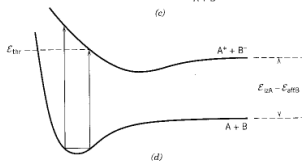
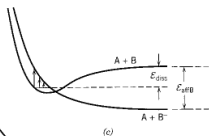
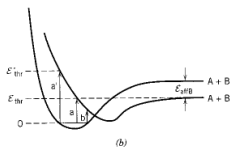
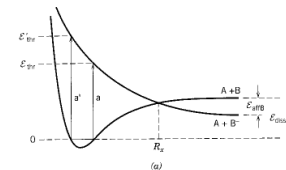
(b)  $AB^-$  bound state  $\Rightarrow a, a'$  dissociative attach. with low energy fragments;  $b$  collision  $AB^{*-} \rightarrow e^- + AB$

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

## 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 IV

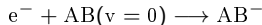
## Electron Impact Detachment



similar to electron-neutral ionization with el. affinity  $\epsilon_{\text{aff}}$  of AB playing the role of the ionization potential BUT the peak in cross section is shifted to energies of  $10\text{--}20\epsilon_{\text{aff}}$  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,

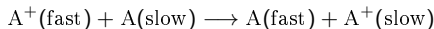
*i. e.* comparable or larger than its vibrational timescale  $10^{-14}$  s  $\Rightarrow$



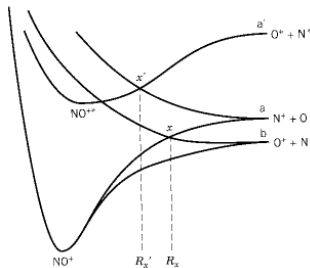
## Heavy-particle collisions - charge transfer

- ▶ 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  $\Delta W$ .
- ▶ 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  $\varepsilon_{\text{thr}}$  and  $\sigma$  can be large at thermal energies.

# Complex reaction schemes for O<sub>2</sub> plasma

Number	Reaction	Rate Constant (cm <sup>3</sup> /s)
<i>Reactions among e, O<sub>2</sub>, O<sub>2</sub><sup>+</sup>, and O<sup>-</sup></i>		
1	e + O <sub>2</sub> momentum transfer	4.7E-8T <sub>e</sub> <sup>0.5</sup>
2	e + O <sub>2</sub> → O <sup>-</sup> + O	8.8E-11 exp(-4.4/T <sub>e</sub> )
3	e + O <sub>2</sub> → 2O + e	4.2E-9 exp(-5.6/T <sub>e</sub> )
4	e + O <sub>2</sub> → O <sub>2</sub> <sup>+</sup> + 2e	9.0E-10T <sub>e</sub> <sup>0.5</sup> exp(-12.6/T <sub>e</sub> )
5	e + O <sup>-</sup> → O + 2e	2.0E-7 exp(-5.5/T <sub>e</sub> )
6	e + O <sub>2</sub> <sup>-</sup> → 2O	5.2E-9/T <sub>e</sub>
7	O <sup>-</sup> + O <sub>2</sub> <sup>-</sup> → O + O <sub>2</sub>	(0.96, 2)E-7(300/T) <sup>0.5</sup>
8	O <sup>-</sup> + O → O <sub>2</sub> + e	(1.4, 5)E-10
9	O <sup>-</sup> + O <sub>2</sub> <sup>-</sup> → 3O	1E-7
<i>Addition of O<sup>+</sup></i>		
10	e + O <sub>2</sub> → O <sup>-</sup> + O <sup>+</sup> + e	7.1E-11T <sub>e</sub> <sup>0.5</sup> exp(-17/T <sub>e</sub> )
11	e + O <sub>2</sub> → O + O <sup>+</sup> + 2e	5.3E-10T <sub>e</sub> <sup>0.5</sup> exp(-20/T <sub>e</sub> )
12	e + O → O <sup>+</sup> + 2e	9.0E-9T <sub>e</sub> <sup>0.7</sup> exp(-13.6/T <sub>e</sub> )
13	O <sup>-</sup> + O <sup>+</sup> → 2O	(2.7, 2)E-7(300/T) <sup>0.5</sup>
14	O <sup>+</sup> + O <sub>2</sub> → O + O <sub>2</sub> <sup>+</sup>	2.0E-11(300/T) <sup>0.5</sup>
<i>Addition of metastable O<sub>2</sub><sup>+</sup>(<sup>1</sup>Δ<sub>g</sub>); see note f below</i>		
15	e + O <sub>2</sub> → O <sub>2</sub> <sup>+</sup> + e	1.7E-9 exp(-3.1/T <sub>e</sub> )
16	e + O <sub>2</sub> <sup>+</sup> → e + O <sub>2</sub>	5.6E-9 exp(-2.2/T <sub>e</sub> )
17	O <sub>2</sub> <sup>+</sup> + O <sub>2</sub> → 2O <sub>2</sub>	2.2E-18(T/300) <sup>0.8</sup>
18	O <sub>2</sub> <sup>+</sup> + O → O <sub>2</sub> + O	(1.0, 7)E-16
<i>Addition of metastable O(<sup>1</sup>D)</i>		
19	e + O <sub>2</sub> → O + O <sup>+</sup> + e	5.0E-8 exp(-8.4/T <sub>e</sub> )
20	e + O → O <sup>+</sup> + e	4.2E-9 exp(-2.25/T <sub>e</sub> )
21	e + O <sup>+</sup> → e + O	8E-9
22	e + O <sup>+</sup> → O <sup>+</sup> + 2e	9.0E-9T <sub>e</sub> <sup>0.7</sup> exp(-11.6/T <sub>e</sub> )
23	O <sup>+</sup> + O → 2O	8.0E-12
24	O <sup>+</sup> + O <sub>2</sub> → O + O <sub>2</sub>	(6.4, 7.0)E-12 exp(67/T)
25	O <sup>+</sup> + O <sub>2</sub> → O + O <sub>2</sub> <sup>+</sup>	1.0E-12
<i>Addition of selected reactions for O<sub>2</sub><sup>-</sup> and O<sub>3</sub></i>		
26	O <sup>-</sup> + O <sub>2</sub> → O <sub>3</sub> + e	5E-15
27	e + O <sub>3</sub> → O <sub>2</sub> <sup>-</sup> + O	1E-9
28	O <sup>-</sup> + O <sub>2</sub> <sup>-</sup> → O <sub>3</sub> + e	3E-10
29	O + O <sub>2</sub> <sup>-</sup> → O <sub>2</sub> <sup>-</sup> + O	1E-10
30	O <sub>2</sub> <sup>-</sup> + O <sub>2</sub> <sup>-</sup> → 2O <sub>2</sub>	2E-7(300/T) <sup>0.5</sup>
31	O <sub>2</sub> <sup>-</sup> + O <sup>+</sup> → O <sub>2</sub> + O	2E-7(300/T) <sup>0.5</sup>
32	O <sub>3</sub> + O <sub>2</sub> → O <sub>2</sub> + O + O <sub>2</sub>	7.3E-10 exp(-11400/T)
33	O <sub>3</sub> + O → 2O <sub>2</sub>	1.8E-11 exp(-2300/T)

Note. T<sub>e</sub> in volts and T in kelvins.

# Complex reaction schemes for O<sub>2</sub> plasma

Number	Reaction	Rate Constant (cm <sup>6</sup> /s)
<i>Reactions among e, O<sub>2</sub>, O<sub>2</sub><sup>+</sup>, and O<sup>-</sup></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	$O + O + O_2 \rightarrow O_2 + O_2$	$2.45E-31 T^{-0.63}$
		$1.3E-32(300/T) \exp(-170/T)$
6	$O + O + O \rightarrow O_2 + O$	$6.2E-32 \exp(-750/T)$
<i>Addition of O<sup>+</sup></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(<sup>1</sup>D)</i>		
12	$O + O^* + O_2 \rightarrow O_2 + O_2$	$9.9E-33$
<i>Addition of selected reactions for metastable O<sub>2</sub><sup>+</sup>(<sup>1</sup>Δ<sub>g</sub>), O<sub>2</sub><sup>-</sup>, and O<sub>3</sub></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	$O_2^- + O_2^+ + O_2 \rightarrow O_2 + O_2 + O_2$	$2E-25(300/T)^{2.5}$

Note. T<sub>e</sub> in volts and T in kelvins; M denotes either O<sub>2</sub> or O. Two values from different sources sometimes given. The notation E-19 means 10<sup>-19</sup>.