Chapter II: Gas phase and collision processes

1. Introduction

In the previous chapter, we considered the behavior of neutral gas. Although cold plasmas involve ionized gases, the degree of ionization of a typical discharge is 10^{-4}
Therefore plasma is typically at neutral ground state that can be described by the gas laws.
Prime features of plasma is that $\approx 10^{18}$ electrons ions-pairs are produced per second.

Collisions phenomena have therefore to be studied.

[1] Basic data of plasma physics. American Institute of Physics, New York. ISBN: 1-56396-296-X.
[2] “Cold Plasma in Materials Fabrications”, A. Grill, IEEE Press, NY(1993). ISBN: 0-7803-1055-1.
[3] “Film deposition by plasma techniques”, M.Konuma, Springer Verlag,(1992). ISBN: 3-540-54057-1.

2. Homogeneous reactions

2.1 Mean free path and reaction rate between two particles

Suppose a particle (a) traveling in a group of particles (b). For a given interaction between particle a and particles b, we have:

$$\lambda_{ab} = \frac{1}{\sigma_{ab}.\tilde{N}_b} \qquad \text{(II.1)}$$

Thus, the collision frequency is

$$\nu_{ab} = \frac{<\vec{V}_a>}{\lambda_{ab}} = <\vec{V}_a>.\sigma_{ab}.\tilde{N}_{ab} \qquad \text{(II.2)}$$

That gives the reaction rate (R):

$$R = <\vec{V}_a>.\sigma_{ab}.\tilde{N}_a.\tilde{N}_b \quad (\mathrm{cm}^3.s)^{-1}$$

$$R = k.\tilde{N}_a.\tilde{N}_b \quad (\mathrm{cm}^3.s)^{-1} \qquad \text{(II.3)}$$

K: is the reaction rate constant ($cm^3\ s^{-1}$).

2. Homogeneous reactions

Detailed modeling of hydrocarbon nanoparticle nucleation in C_2H_2 discharge

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RF // plate, 13.56 MHz, simulation

DETAILED MODELING OF HYDROCARBON… PHYSICAL REVIEW E **73**, 026405 (2006)

TABLE III. Ion-molecule processes taken into account in the fluid model. The abbreviation "est." stands for estimated, and "calc." for calculated.

	Reaction	Rate constant ($m^3\ s^{-1}$)	Comment	Reference
	Cluster growth through hydrocarbon anions ($C_{2n}H^-$) with C_2H_2			
1.	$C_2H^- + C_2H_2 \rightarrow C_4H^- + H_2$	1.0×10^{-18}	est.	[14]
2.	$C_4H^- + C_2H_2 \rightarrow C_6H^- + H_2$	1.0×10^{-18}	est.	[14]
3.	$C_{2n}H^- + C_2H_2 \rightarrow C_{2n+2}H^- + H_2$	1.0×10^{-18}	$n=3,\ldots,5$,est.	[14]
	Cluster growth through hydrocarbon cations ($C_{2n}H_m^+$) with C_2H_2 or H_2			
4.	$H_2^+ + C_2H_2 \rightarrow C_2H_2^+ + H_2$	5.3×10^{-15}		[41]
5.	$C_2H^+ + H_2 \rightarrow C_2H_2^+ + H$	1.7×10^{-15}		[41]
6.	$C_2H^+ + C_2H_2 \rightarrow C_4H_2^+ + H$	1.2×10^{-15}		[42]
7.	$C_2H_2^+ + C_2H_2 \rightarrow C_4H_2^+ + H_2$	1.2×10^{-15}		[42]
8.	$C_4H_2^+ + C_2H_2 \rightarrow C_6H_4^+$	1.4×10^{-16}		[41]
9.	$C_6H_2^+ + C_2H_2 \rightarrow C_8H_4^+$	1.0×10^{-17}		[42]
10.	$C_6H_4^+ + C_2H_2 \rightarrow C_8H_6^+$	1.0×10^{-16}	est.	[42]
11.	$C_8H_4^+ + C_2H_2 \rightarrow C_{10}H_6^+$	1.0×10^{-16}	est.	[42]
12.	$C_8H_6^+ + C_2H_2 \rightarrow C_{10}H_6^+ + H_2$	1.0×10^{-16}	est.	[42]
13.	$C_{10}H_6^+ + C_2H_2 \rightarrow C_{12}H_6^+ + H_2$	1.0×10^{-16}	est.	[42]
	Neutralization reactions of hydrocarbon anions with H_2^+ and $C_{2n}H_m^+$			
14.	$C_{2n}H^- + H_2^+ \rightarrow C_{2n}H + H + H$	$\sim1.7\times10^{-13}$	$n=1,\ldots,6$ calc.	[43]
15.	$C_{2n}H^- + C_{2n}H_m^+ \rightarrow C_{2n}H + C_{2n}H_m$	$\sim4.0\times10^{-14}$	$n=1,\ldots,6$ calc.	[43]

2. Homogeneous reactions

2.2 Type of collisions

Particles have two types of energy: *kinetic* and *potential*

Kinetic: related to motion. An increase = increase of speed

Potential: related to electronic structure of the colliding ions, atoms, molecules, …. An increase is manifested by ionization and other excitation processes.

An elastic collision is one in which there is an interchange of kinetic energy only.

- There are conservation of momentum and kinetic energy of translation motion.
- No excitation occurs

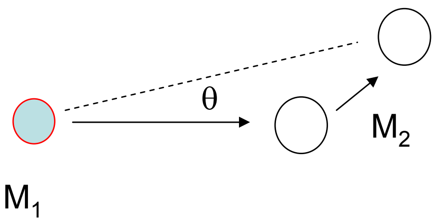
Example: billiard: only kinetic energy is exchanged

An inelastic collision has no such restriction: there is generally an increase in potential energy:

- Excitation
- Ionization

2. Homogeneous reactions

Elastic collisions



$$\frac{E_2}{E_1} = \frac{4.M_1.M_2}{(M_1+M_2)^2}.\cos^2\theta \qquad \text{(II.4)}$$

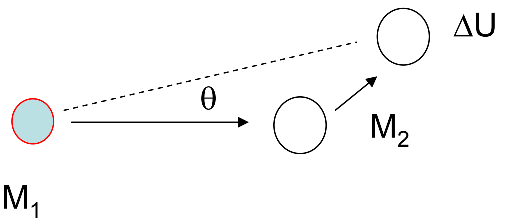
$\theta = 0$

If $M_1 = M_2$ ☞ $E_2/E_1=1$
Max energy is transferred (After collision, M_1 is at rest, M_2 is moving).

If $M_1 << M_2$ (e.g. e → ion) ☞ $K = 4.M_1 / M_2 \approx 10^{-4}$.

Electrons do not transfert kinetic energy in elastic mode

Inelastic collisions



$$\frac{\Delta U}{E_1} = \frac{M_2}{(M_1+M_2)}.\cos^2\theta \qquad \text{(II.5)}$$

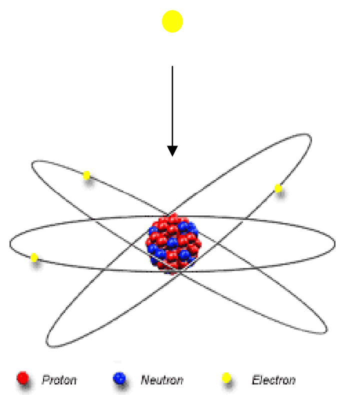
$\theta = 0$

If $M_1 << M_2$ (e.g. e → ion)

$$\frac{\Delta U}{E_1} \approx 1$$

All the electron kinetic energy is transferred to the heavier species in inelastic collision

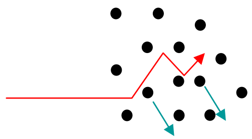
2.3 Electron collisions



é + A → é + A*
é + A_2 → é + A_2*
é + AB → é + AB*

Elastic collisions

Deviation



Inelastic collisions

Excitation

Ionization

Electron attachement and dissociation

2.3 Electron collisions

Excitation

$$é + A \rightarrow é + A^*$$
$$é + A_2 \rightarrow é + A_2^*$$
$$é + AB \rightarrow é + AB^*$$

If de-excitation in 10^{-8} s: glow
If longer: metastable

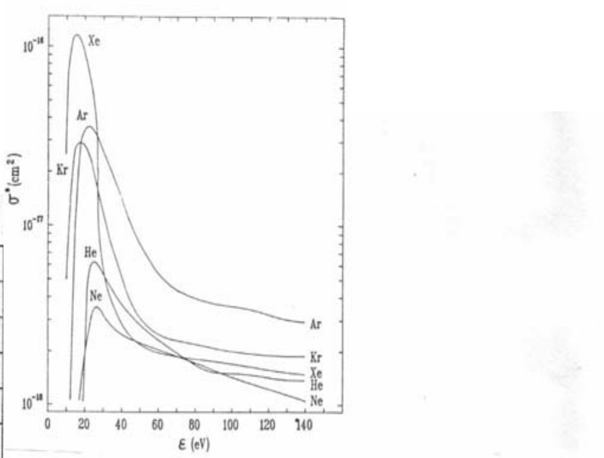


Fig.2.14. Total cross section for metastable production in noble gases by elec impact [2.13]

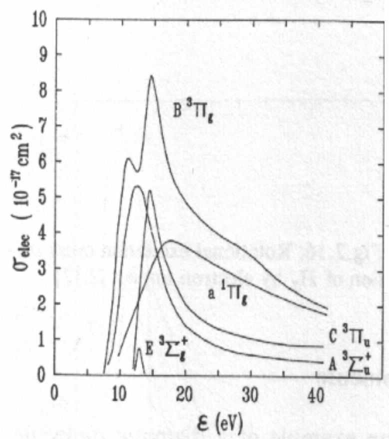


Fig.2.19. Electronic excitation cross section of N_2 by electron impact [2.26]

2. Homogeneous reactions

2.3 Electron collisions

Ionization

$$e + Ar \rightarrow 2\,é + Ar^+$$

↓ will produce new ionizations.

Energy requirements:

$K > V_i$ (V_i: Ioniz. potential of the atom/molecule)

Ionization potential of atoms and molecules [2]		
Neutral	Ion	Ionization Potential (eV)
Si	Si^+	8.1
CH_4	CH_4^+	13
C_2H_2	$C_2H_2^+$	11.4
H_2	H_2^+	15.4
N_2	N_2^+	15.6
O_2	O_2^+	12.2
H_2O	H_2O^+	12.6
SiH_4	SiH_4^+	12.2

2. Homogeneous reactions

Electron impact treshold in C_2H_2 discharge

DETAILED MODELING OF HYDROCARBON… PHYSICAL REVIEW E 73, 026405 (2006)

TABLE II. The electron impact collisions and their corresponding threshold energies considered in the 1D fluid model. The abbreviation "est." stands for estimated.

	Reaction	Threshold energy (eV)	Reaction type	Reference
1.	$C_2H_2+e^- \rightarrow C_2H_2^+ + 2e^-$	11.4	Ionization	[30]
2.	$C_2H_2+e^- \rightarrow C_2H^+ + H + 2e^-$	16.5	Dissociative ionization	[30]
3.	$C_2H_2+e^- \rightarrow C_2^+ + H_2 + 2e^-$	17.5	Dissociative ionization	[30]
4.	$C_2H_2+e^- \rightarrow CH^+ + CH + 2e^-$	20.6	Dissociative ionization	[30]
5.	$C_2H_2+e^- \rightarrow C^+ + CH_2 + 2e^-$	20.3	Dissociative ionization	[30]
6.	$C_2H_2+e^- \rightarrow H^+ + C_2H + 2e^-$	18.4	Dissociative ionization	[30]
7.	$C_2H_2^{(0)}+e^- \rightarrow C_2H_2^{(\nu=5)} + e^-$	0.09	Vibrational excitation	[31]
8.	$C_2H_2^{(0)}+e^- \rightarrow C_2H_2^{(\nu=2)} + e^-$	0.29	Vibrational excitation	[31]
9.	$C_2H_2^{(0)}+e^- \rightarrow C_2H_2^{(\nu=3)} + e^-$	0.41	Vibrational excitation	[31]
10.	$C_2H_2+e^- \rightarrow C_2H + H + e^-$	7.5	Dissociation	[30]
11.	$C_2H_2+e^- \rightarrow C_2H^- + H$	1.66	Dissociative attachment	[32]
12.	$H_2+e^- \rightarrow H_2^+ + 2e^-$	15.4	Ionization	[33]
13.	$H_2+e^- \rightarrow H_2^{(\nu=1)} + e^-$	0.54	Vibrational excitation	[34]
14.	$H_2+e^- \rightarrow H_2^{(\nu=2)} + e^-$	1.08	Vibrational excitation	[34]
15.	$H_2+e^- \rightarrow H_2^{(\nu=3)} + e^-$	1.62	Vibrational excitation	[34]
16.	$H_2+e^- \rightarrow H + H + e^-$	8.9	Dissociation	[35]
17.	$C_4H_2+e^- \rightarrow C_4H + H + e^-$	7.5	Dissociation	[30], est.
18.	$C_6H_2+e^- \rightarrow C_6H + H + e^-$	7.5	Dissociation	[30], est.
19.	$C_8H_2+e^- \rightarrow C_8H + H + e^-$	7.5	Dissociation	[30], est.
20.	$C_{10}H_2+e^- \rightarrow C_{10}H + H + e^-$	7.5	Dissociation	[30], est.
21.	$C_{12}H_2+e^- \rightarrow C_{12}H + H + e^-$	7.5	Dissociation	[30], est.
22.	$C_4H_2+e^- \rightarrow C_4H_2^+ + 2e^-$	11.4	Ionization	[30], est.
23.	$C_6H_2+e^- \rightarrow C_6H_2^+ + 2e^-$	11.4	Ionization	[30], est.

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2. Homogeneous reactions

2.3 Electron collisions

Ionization

Ionization potential of atoms [3]					
Atom	1	2	3	4	5
H	13.598				
He	24.586	54.416			
N	14.534	29.601	47.887	77.471	97.888
O	13.618	35.116	54.934	77.412	113.896
F	17.423	34.98	62.646	87.14	114.214
Cl	12.967	23.80	39.9	53.5	67.8
Ar	15.759	27.629	40.74	59.81	75.02

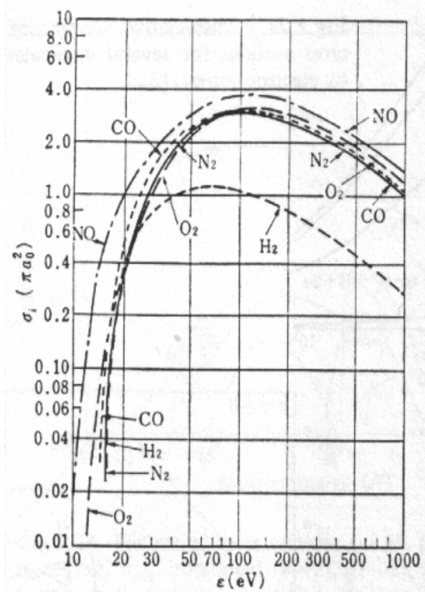


Fig.2.20. Total ionization cross section of gas molecules by electron impact [2.11]

$\pi . a_0^2 = 8.82 x 10^{-17}$ cm^2

a0: radius of the first orbit of hydrogen

2.3 Electron collisions

Electron attachment and dissociation

When an electron collides with a neutral gas molecule, it can be captured to form negative ions.
Negative ions return to neutral atom or molecule through dissociation, i.e. breaking apart if molecules.

é + AB	$\rightarrow$ A + B^-	(Diss. Attachm. or capture)
é + A_2	$\rightarrow$ A^+ + A^- + é	(Diss. Ionization)
é + AB	$\rightarrow$ A^+ + B^- + é	(Ion pair formation)
é + A_2	$\rightarrow$ 2 A + é	(Dissociation)
é + AB	$\rightarrow$ é + A + B	

Only if $E_é$ > treshold value (H_2:8.8, N_2: 9.4 eV)

Exemple:

é + O_2 $\rightarrow$ 2 O + é $\rightarrow$ O + O^- (a)

é + CF_4 $\rightarrow$ CF_3 + F + é $\rightarrow$ CF_3 + F^- (b)

Reaction a: used for stripping photoresist in micro-electronic processes. Atomic oxygen is produced, and reacts very easily with polymers to form CO, CO_2 and H_2O.

Reaction b: plasma etching of Si, SiO_2, Si_3N_4.

2. Homogeneous reactions

2.3 Electron collisions *Electron attachment and dissociation*

Cross section for dissociative capture and electron energy at the maximum [2]

Molecule	Ion	W (eV)	σ (10^{-17} cm^2)
HI	I^-	0	2300
I_2	I^-	0.3	300
HBr	Br^-	0.28	27
HCl	Cl^-	0.81	1.99
O_2	O^-	6.7	0.143
CO_2	O^-	8.03	0.0482
H_2O	H^-	8.6	0.13
H_2	H^-	3.75	0.000016

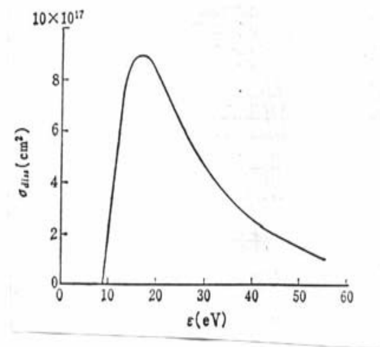
Cross section for formation of neutral and positively charged fragments from CH_4 by collision with 100 eV electrons [2]

Positive Ions		Neutral fragments	
Ion	σ (x10^{-16} cm^2)	Species	σ (x10^{-16} cm^2)
H^+	0.04	H	2.4
H_2^+	0.02	H_2	0.8
C^+	0.05	C	-
CH^+	0.28	CH	0.1
CH_2^+	0.28	CH_2	0.2
CH_3^+	1.5	CH_3	1.2
CH_4^+	1.8		

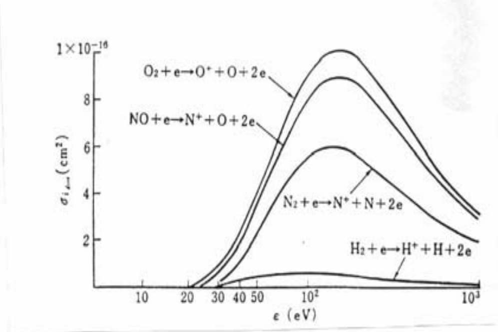
2. Homogeneous reactions

2.3 Electron collisions

Electron attachment and dissociation



Dissociation cross section of H_2 by electron impact



Dissociative ionization cross section for several molecules by electron impact.

2. Homogeneous reactions

2.3 Electron collisions

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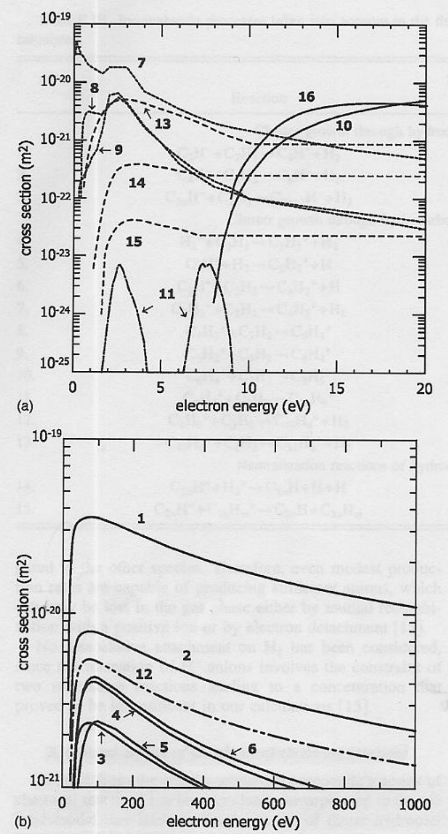


FIG. 2. Cross sections of the electron impact collisions of C_2H_2 and H_2: (a) vibrational excitation, dissociation, and dissociative attachment; (b) electron impact ionization. The number on each curve refers to the reaction number specified in Table II. Curves 1 and 10 have also been used as an approximation for the unknown cross sections of reactions 22,23 and 17–21, respectively (see text).

2. Homogeneous reactions

2.3 Electron collisions

Total cross-section

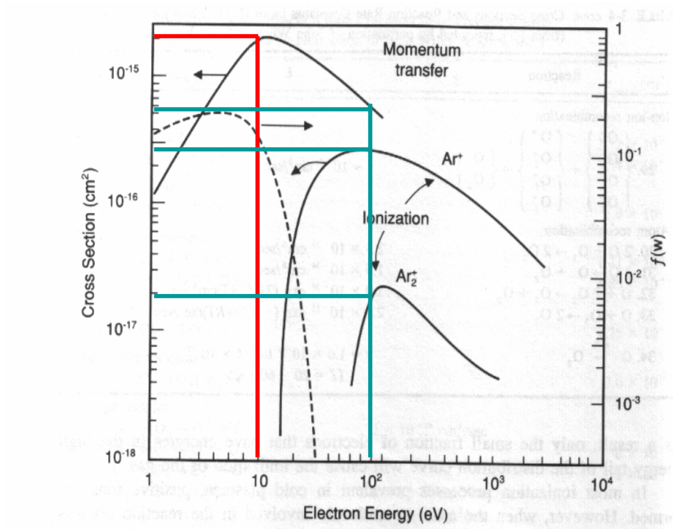


Fig. 3-3 Cross sections versus electron energy (—) and Druyvesteyn energy distribution for $T_e = 5$ eV (- -).

- 10 eV, RT, 5×10^{-3} Torr, purely elastic σ: 2×10^{-15} /cm²

$$\tilde{N} = 9.65\,10^{18}\,\frac{p\,(\mathrm{Torr})}{T\,(^\circ K)} = 1.6\times10^{20}\ \mathrm{at/cm^3} \Rightarrow \lambda_{ab} = \frac{1}{\sqrt{2}.\sigma_{ab}.\tilde{N}_b} = 2.1\ \mathrm{cm}$$

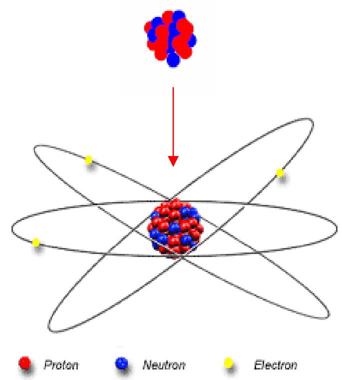
- 100 ev: $\sigma_{elastic}$: 5×10^{-16}, σ_{Ar+}:2×10^{-16}, σ_{Ar++}:2×10^{-17}

$$\lambda_{ab} = \frac{1}{\sqrt{2}.\sigma_{ab}.\tilde{N}_b} = 6\ \mathrm{cm}$$

But: energy distribution

2. Homogeneous reactions

2.3 Ion and neutral collisions



2.4.1 Ion - Neutral.

$B_2 + A^+ \rightarrow B_2^+ + A$

$A^+ + BC \rightarrow A + BC^+$

$A^+ + BC \rightarrow A + B^+ + C$

2.4.2 Ion - Ion.

$A^+ + B^- \rightarrow AB + hv$

(Recombination)

2.4.3 Neutral-Neutral.

$A + B \rightarrow A^+ + B-$ (Rare in a cold plasma)

2.4.4 Penning effect.

$B^* + A \rightarrow A^+ + B + e$

$B^* + A_2 \rightarrow 2A + B$

Ex: $Ne + e \rightarrow Ne^* + e$

$Ne^* + Ar \rightarrow Ne + Ar^+ + e$

This reaction is much more likely than Ne + é $\rightarrow$ Ne^+ + é.

☞Ar acts as a catalyst.

During sputter deposition, the observed metal ions are due to penning ionization induced by excited noble gas atoms

2. Homogeneous reactions

2.3 Ion and neutral collisions

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	Reaction	Rate constant ($m^3 s^{-1}$)	Comment	Reference
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1.	$C_2H^- + C_2H_2 \rightarrow C_4H^- + H_2$	1.0×10^{-18}	est.	[14]
2.	$C_4H^- + C_2H_2 \rightarrow C_6H^- + H_2$	1.0×10^{-18}	est.	[14]
3.	$C_{2n}H^- + C_2H_2 \rightarrow C_{2n+2}H^- + H_2$	1.0×10^{-18}	$n=3,\ldots,5$,est.	[14]
	Cluster growth through hydrocarbon cations ($C_{2n}H_m{}^+$) with C_2H_2 or H_2			
4.	$H_2{}^+ + C_2H_2 \rightarrow C_2H_2{}^+ + H_2$	5.3×10^{-15}		[41]
5.	$C_2H^+ + H_2 \rightarrow C_2H_2{}^+ + H$	1.7×10^{-15}		[41]
6.	$C_2H^+ + C_2H_2 \rightarrow C_4H_2{}^+ + H$	1.2×10^{-15}		[42]
7.	$C_2H_2{}^+ + C_2H_2 \rightarrow C_4H_2{}^+ + H_2$	1.2×10^{-15}		[42]
8.	$C_4H_2{}^+ + C_2H_2 \rightarrow C_6H_4{}^+$	1.4×10^{-16}		[41]
9.	$C_6H_2{}^+ + C_2H_2 \rightarrow C_8H_4{}^+$	1.0×10^{-17}		[42]
10.	$C_6H_4{}^+ + C_2H_2 \rightarrow C_8H_6{}^+$	1.0×10^{-16}	est.	[42]
11.	$C_8H_4{}^+ + C_2H_2 \rightarrow C_{10}H_6{}^+$	1.0×10^{-16}	est.	[42]
12.	$C_8H_6{}^+ + C_2H_2 \rightarrow C_{10}H_6{}^+ + H_2$	1.0×10^{-16}	est.	[42]
13.	$C_{10}H_6{}^+ + C_2H_2 \rightarrow C_{12}H_6{}^+ + H_2$	1.0×10^{-16}	est.	[42]
	Neutralization reactions of hydrocarbon anions with $H_2{}^+$ and $C_{2n}H_m{}^+$			
14.	$C_{2n}H^- + H_2{}^+ \rightarrow C_{2n}H + H + H$	$\sim1.7\times10^{-13}$	$n=1,\ldots,6$ calc.	[43]
15.	$C_{2n}H^- + C_{2n}H_m{}^+ \rightarrow C_{2n}H + C_{2n}H_m$	$\sim4.0\times10^{-14}$	$n=1,\ldots,6$ calc.	[43]

2. Homogeneous reactions

2.3 Molecule-molecule collisions

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TABLE IV. Molecule-molecule processes taken into account in the fluid model.

	Reaction	Rate constant ($m^3 s^{-1}$)	Comment	Reference
	Cluster growth through C_2H insertion			
1.	$C_2H + H_2 \rightarrow C_2H_2 + H$	4.9×10^{-19}	$1.82\times10^{-17}\exp(-1443/T)$	[24]
2.	$C_2H + H \rightarrow C_2H_2$	4.1×10^{-16}	$1.66\times10^{-13}T^{-1}$	[25]
3.	$C_2H + C_2H_2 \rightarrow C_4H_2 + H$	5.8×10^{-17}		[24]
4.	$C_2H + C_4H_2 \rightarrow C_6H_2 + H$	6.6×10^{-17}		[24]
5.	$C_2H + C_{2n}H_2 \rightarrow C_{2n+2}H_2 + H$	5.0×10^{-17}	$n=3,\ldots,5$	[18], est.
	Hydrogen insertion			
6.	$H + C_2H_2 \rightarrow C_2H_3$	3.5×10^{-19}	$7.25\times10^{-18}\exp(-1212.7/T)$	[44]
7.	$H + C_4H_2 \rightarrow C_4H_3$	1.2×10^{-18}	$2.82\times10^{+19}T^{-11.67}\exp(-6441/T)$	[25]
8.	$H + C_6H_2 \rightarrow C_6H_3$	1.6×10^{-18}	$7.1\times10^{+15}T^{-10.15}\exp(-6667.6/T)$	[25]
9.	$H + C_{2n}H \rightarrow C_{2n}H_2$	4.1×10^{-16}	$1.66\times10^{-13}T^{-1}$; $n=2,\ldots,6$	[25]
10.	$C_{2n}H + H_2 \rightarrow C_{2n}H_2 + H$	4.9×10^{-19}	$1.82\times10^{-17}\exp(-1443/T)$; $n=2,\ldots,6$	[24]
	Hydrogen abstraction			
11.	$H + C_2H_3 \rightarrow H_2 + C_2H_2$	6.6×10^{-17}		[44,45]
12.	$H + C_4H_3 \rightarrow H_2 + C_4H_2$	2.4×10^{-17}		[25]
13.	$H + C_6H_3 \rightarrow H_2 + C_6H_2$	6.6×10^{-17}	$k=k_{reac11}$	[44], est.
	Cluster growth through acetylene insertion			
14.	$C_4H + C_2H_2 \rightarrow C_6H_2 + H$	6.6×10^{-17}		[24]
15.	$C_{2n}H + C_2H_2 \rightarrow C_{2n+2}H_2 + H$	6.6×10^{-17}	$k=k_{reac14}$; $n=3,\ldots,5$	[24], est.
	Other neutral-neutral reactions			
16.	$CH + H_2 \rightarrow CH_2 + H$	1.0×10^{-18}	$1.82\times10^{-22}T^{1.79}\exp(-840.4/T)$	[25]
17.	$CH_2 + H \rightarrow CH + H_2$	2.7×10^{-16}		[44,46]
18.	$CH_2 + CH_2 \rightarrow C_2H_2 + H_2$	5.3×10^{-17}		[25,47]
19.	$C_2H + C_2H_3 \rightarrow C_2H_2 + C_2H_2$	5.0×10^{-17}		[48]
20.	$CH_2 + CH \rightarrow C_2H_2 + H$	6.6×10^{-17}		[25]
21.	$C_2H_2 + C_2H \rightarrow C_4H_3$	2.2×10^{-18}	$1.82\times T^{-6.3}\exp(-1404/T)$	[25]
22.	$C_4H_2 + C_2H \rightarrow C_6H_3$	2.2×10^{-18}	$k=k_{reac21}$	[25], est.
23.	$C_2H_3 + CH \rightarrow C_2H_2 + CH_2$	8.3×10^{-17}		[48]
24.	$C_4H_3 + H \rightarrow C_2H_2 + C_2H_2$	1.1×10^{-16}	$2.65\times10^{-11}T^{-1.6}\exp(-1117/T)$	[25]
25.	$C_6H_3 + H \rightarrow C_4H_2 + C_2H_2$	8.1×10^{-17}	$3.98\times10^{-11}T^{-1.6}\exp(-1409/T)$	[25]

2. Homogeneous reactions

2.3 Oxygen plasma case

TABLE 3-4 Cross Sections and Reaction Rate Constants in an Oxygen Plasma (from [5], reprinted by permission of John Wiley & Sons, Inc.)

Reaction	k	σ_{max} (cm^2)
Ionization		
1. $e + O_2 \rightarrow O_2^+ + 2e$		2.72×10^{-16}
2. $e + O \rightarrow O^+ + 2e$		1.54×10^{-18}
Dissociative ionization		
3. $e + O_2 \rightarrow O^+ + O$		1.0×10^{-16}
Dissociative attachment		
4. $e + O_2 \rightarrow O^- + O$		1.41×10^{-18}
5. $e + O_2 \rightarrow O^- + O + e$		4.85×10^{-19}
Dissociation		
6. $e + O_2 \rightarrow 2\,O + e$		2.25×10^{-18}
Metastable formation		
7. $e + O_2 \rightarrow O_2(^1\Delta_g) + e$		3.0×10^{-20}
Charge transfer		
8. $O^+ + O_2 \rightarrow O_2^+ + O$	2×10^{-11} cm^3/sec	
9. $O_2^+ + O \rightarrow O + O_2$		8×10^{-16}
10. $O_2^+ + O_2 \rightarrow O_3^+ + O$		1×10^{-16}
11. $O_2^+ + 2\,O_2 \rightarrow O_4^+ + O_2$	2.8×10^{-30} cm^6/sec	
12. $O^- + O_2 \rightarrow O_2^- + O$	2.5×10^{-14} cm^3/sec at E/p = 20 V/cm torr; 3.4×10^{-12} cm^3/sec at E/p = 45 V/cm torr	
13. $O^- + O_3 \rightarrow O_3^- + O$	5.3×10^{-10} cm^3/sec	
14. $O^- + 2\,O_2 \rightarrow O_3^- + O_2$	$1.0 \pm 0.2 \times 10^{-30}$ cm^6/sec	
15. $O_2^- + O \rightarrow O^- + O_2$	5×10^{-10} cm^3/sec	
16. $O_2^- + O_2 \rightarrow O_3^- + O$		$< 10^{-18}$
17. $O_2^- + O_3 \rightarrow O_3^- + O_2$	4.0×10^{-10} cm^3/sec	
18. $O_2^- + 2\,O_2 \rightarrow O_4^- + O_2$	3×10^{-31} cm^6/sec	
19. $O_3^- + O_2 \rightarrow O_2^- + O_3$		4×10^{-17}
20. $O_4^- + O \rightarrow O_3^- + O_2$	4×10^{-10} cm^3/sec	
21. $O_4^- + O_2 \rightarrow O_2^- + 2\,O_2$	6×10^{-15} cm^3/sec	
Detachment		
22. $O^- + O \rightarrow O_2 + e$	3.0×10^{-10} cm^3/sec	
23. $O^- + O_2 \rightarrow O + O_2 + e$		7×10^{-16}
24. $O^- + O_2(^1\Delta_g) \rightarrow O_3 + e$	$\sim 3 \times 10^{-10}$ cm^3/sec	
25. $O_2^- + O \rightarrow O_3 + e$	5.0×10^{-10} cm^3/sec	
26. $O_2^- + O_2 \rightarrow 2\,O_2 + e$		7×10^{-16}
27. $O_2^- + O_2(^1\Delta_g) \rightarrow 2\,O_2 + e$	$\sim 2 \times 10^{-10}$ cm^3/sec	
Electron-ion recombination		
28. $e + \begin{Bmatrix} O \\ O_2^+ \\ O_3^+ \\ O_4^+ \end{Bmatrix} \rightarrow \begin{Bmatrix} O \\ 2\,O \\ O + O_2 \\ 2\,O_2 \end{Bmatrix}$	$\lesssim 10^{-7}$ cm^3/sec	
Ion-ion recombination		
29. $\begin{Bmatrix} O^- \\ O_2^- \\ O_3^- \\ O_4^- \end{Bmatrix} + \begin{Bmatrix} O^+ \\ O_2^+ \\ O_3^+ \\ O_4^+ \end{Bmatrix} \rightarrow \begin{Bmatrix} O \\ O_2 \end{Bmatrix}$	$\sim 10^{-7}$ cm^3/sec	
Atom recombination		
30. $2\,O + O_2 \rightarrow 2\,O_2$	2.3×10^{-33} cm^6/sec	
31. $3\,O \rightarrow O + O_2$	1.5×10^{-34} cm^6/sec	
32. $O + 2\,O_2 \rightarrow O_3 + O_2$	1.9×10^{-35} exp $(2100/RT)$ cm^6/sec	
33. $O + O_3 \rightarrow 2\,O_2$	2.0×10^{-11} exp $(-4790/RT)$ cm^3/sec	
34. $O \xrightarrow{wall} O_2$	$\gamma = 1.6 \times 10^{-4}$ to 1.4×10^{-2} (T = 20 – 600 °C)	

$$R \quad = k.\tilde{N}$$

3. Heterogenous reactions

Interaction of a solid surface with atoms (A,B), monomer molecules (M), radicals (R) and polymers (P) formed in a plasma.

3.1 Adsorption

$M_g + S \rightarrow M_s$

$R_g + S \rightarrow R_s$

3.2 Recombination or compounds formation

Deposition $A_{on\ S} + A \rightarrow S + A_2$

Etching $R_{on\ S} + R_1 \rightarrow S + M$

Energy is released at the surface,

Rate of surface recombination depends on the catalytic properties of the surface:

$\sigma(F + F \rightarrow F_2$ on Teflon$) \approx 1/100\ \sigma\ (F + F \rightarrow F_2$ on Cu$)$

3.3 Polymerisation

$R_g + R_s \rightarrow P_s$

$M_g + R_s \rightarrow P_s'$

3.4 Sputtering

$B_{on\ S} + A^+ \rightarrow Surf^+ + B + A$

Indices g and s = gas or solid phase