Plasma physics

2023 winter s. 2/1 , C+Ex

prof. Juraj Glosík, doc. Radek Plašil

- Chemical reactions in the plasma
- Introduction to gas discharges: Townsend regime, Corona, Streamers

Example of simple chemical kinetics—H_2

$$\begin{aligned} H_2 + h\nu &\rightarrow H + H \\ &\rightarrow H_2^+ + e^- \\ &\rightarrow H^- + H^+ \end{aligned}$$

$$\begin{aligned} H_2 + e^- &\rightarrow H + H + e^- \\ &\rightarrow H_2^+ + e^- + e^- \\ &\rightarrow H^- + H \end{aligned}$$

$$H_2 + H \rightarrow H + H + H$$

$$H + e^- \rightarrow H^- + h\nu$$

$$H + e^- \rightarrow H^+ + e^- + e^-$$

$$H_2^+ + h\nu \rightarrow H^+ + H$$

$$H_2^+ + H \rightarrow H_2 + H^+$$

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

$$H_2^+ + H^- \rightarrow H_2 + H$$

$$\begin{aligned} H_2^+ + e^- &\rightarrow H_2 + h\nu \\ &\rightarrow H + H \end{aligned}$$

$$H^+ + e^- \rightarrow H + h\nu$$

$$H^+ + H_2 \rightarrow H_3^+ + h\nu$$

$$H^+ + 2\,H_2 \rightarrow H_3^+ + H_2$$

$$H^+ + H^- \rightarrow H + H$$

$$H_3^+ + h\nu \rightarrow H_2^+ + H$$

$$\begin{aligned} H_3^+ + e^- &\rightarrow H_2^+ + H \\ &\rightarrow H + H + H \end{aligned}$$

$$H_3^+ + H_2 \rightarrow H_5^+$$

…

…

…

Vibrational, rotational states

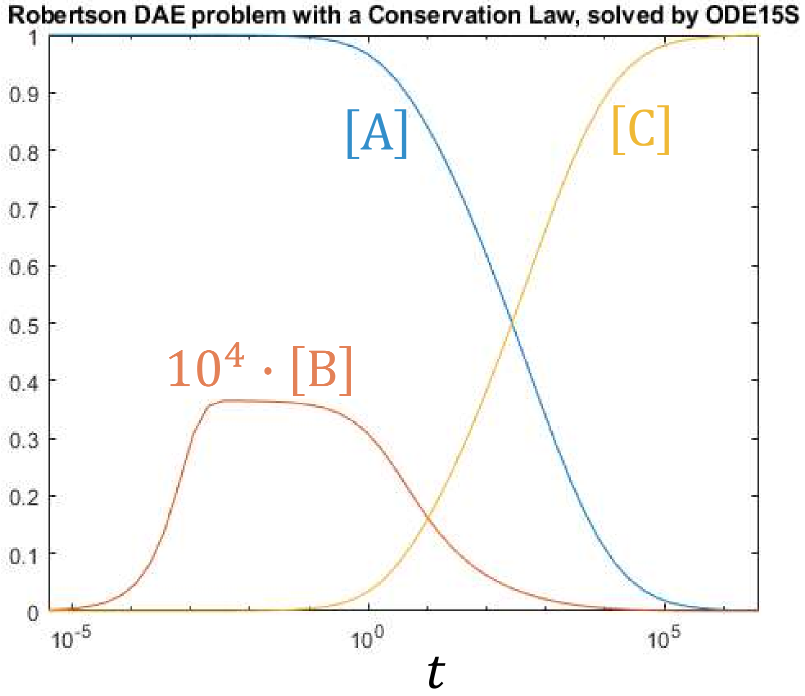
Isotopologues (Deuteration)

Robertson's model "STIFF" – ROBER problem

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \qquad k_1 = 0.04 \qquad [\mathrm{A}]_0 = 1$$

$$\mathrm{B} + \mathrm{B} \xrightarrow{k_2} \mathrm{C} + \mathrm{B} \qquad k_2 = 3 \cdot 10^7 \qquad [\mathrm{B}]_0 = 0$$

$$\mathrm{B} + \mathrm{C} \xrightarrow{k_3} \mathrm{A} + \mathrm{C} \qquad k_3 = 1 \cdot 10^4 \qquad [\mathrm{C}]_0 = 0$$


Robertson DAE problem with a Conservation Law, solved by ODE15S

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_1[\mathrm{A}] + k_3[\mathrm{B}][\mathrm{C}]$$

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = +k_1[\mathrm{A}] - k_2[\mathrm{B}]^2 - k_3[\mathrm{B}][\mathrm{C}]$$

$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = +k_2[\mathrm{B}]^2$$

$$\begin{pmatrix} \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} \\ \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} \\ \frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} \end{pmatrix} = \begin{pmatrix} -k_1 & 0 & +k_3[\mathrm{B}] \\ +k_1 & -k_2[\mathrm{B}] & -k_3[\mathrm{B}] \\ 0 & +k_2[\mathrm{B}] & 0 \end{pmatrix} \begin{pmatrix} [\mathrm{A}] \\ [\mathrm{B}] \\ [\mathrm{C}] \end{pmatrix}$$

Databases for plasma chemistry

A Kinetic Database For Astrochemistry (KIDA)

kida.astrochem-tools.org

Wakelam V. et al. *ApJS* 199 (2012) 21
doi: 10.1088/0067-0049/199/1/21

species 713
reactions > 8800

The UMIST Database for Astrochemistry

udfa.ajmarkwick.net

Millar T. J. et al. “The UMIST Database for Astrochemistry 2022”
https://doi.org/10.48550/arXiv.2311.03936

species 737
reactions 8767

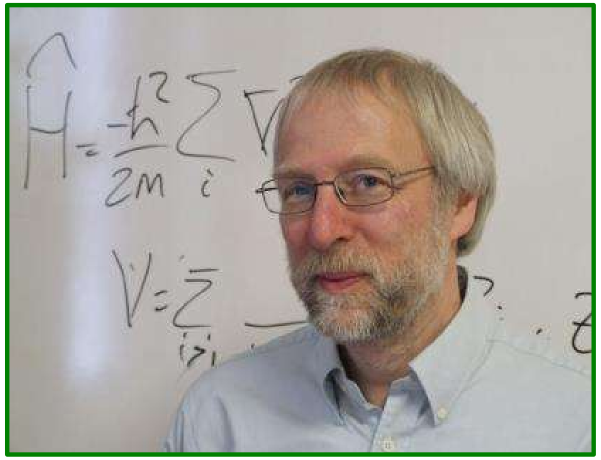
Databases for plasma chemistry QuantemolDB

www.quantemolDB.com

plasma chemistry

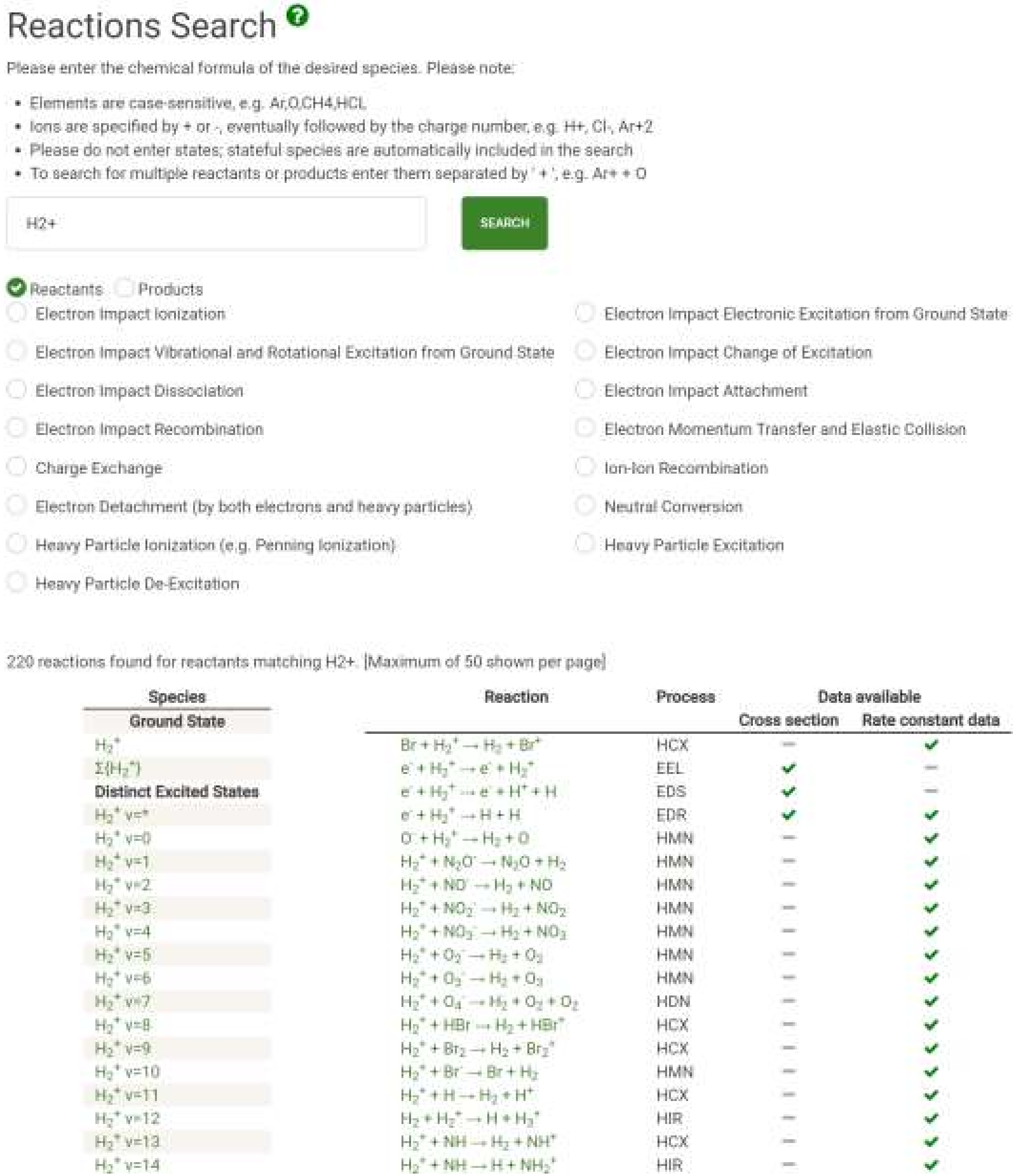
Quantemol

species 2 485
reactions 28 917
+ surface processes



Prof. Jonathan Tennyson, FRS, UCL

Tennyson J. et al. *Plasma Sources Sci. Technol.* 31 (2022) 095020
doi: 10.1088/1361-6595/ac907e



Reactions Search

Please enter the chemical formula of the desired species. Please note:

- Elements are case-sensitive, e.g. Ar,O,CH4,HCL
- Ions are specified by + or -, eventually followed by the charge number, e.g. H+, Cl-, Ar+2
- Please do not enter states; stateful species are automatically included in the search
- To search for multiple reactants or products enter them separated by ' + ', e.g. Ar+ + O

H2+

● Reactants ○ Products

○ Electron Impact Ionization
○ Electron Impact Vibrational and Rotational Excitation from Ground State
○ Electron Impact Dissociation
○ Electron Impact Recombination
○ Charge Exchange
○ Electron Detachment (by both electrons and heavy particles)
○ Heavy Particle Ionization (e.g. Penning Ionization)
○ Heavy Particle De-Excitation
○ Electron Impact Electronic Excitation from Ground State
○ Electron Impact Change of Excitation
○ Electron Impact Attachment
○ Electron Momentum Transfer and Elastic Collision
○ Ion-Ion Recombination
○ Neutral Conversion
○ Heavy Particle Excitation

220 reactions found for reactants matching H2+. [Maximum of 50 shown per page]

Species
Ground State
H_2^+
$\Sigma(H_2^+)$
Distinct Excited States
H_2^+ v=*
H_2^+ v=0
H_2^+ v=1
H_2^+ v=2
H_2^+ v=3
H_2^+ v=4
H_2^+ v=5
H_2^+ v=6
H_2^+ v=7
H_2^+ v=8
H_2^+ v=9
H_2^+ v=10
H_2^+ v=11
H_2^+ v=12
H_2^+ v=13
H_2^+ v=14

Reaction	Process	Data available	
		Cross section	Rate constant data
$Br + H_2^+ \rightarrow H_2 + Br^+$	HCX	–	✓
$e^- + H_2^+ \rightarrow e^- + H_2^+$	EEL	✓	–
$e^- + H_2^+ \rightarrow e^- + H^+ + H$	EDS	✓	–
$e^- + H_2^+ \rightarrow H + H$	EDR	✓	✓
$O^- + H_2^+ \rightarrow H_2 + O$	HMN	–	✓
$H_2^+ + N_2O^- \rightarrow N_2O + H_2$	HMN	–	✓
$H_2^+ + NO^- \rightarrow H_2 + NO$	HMN	–	✓
$H_2^+ + NO_2^- \rightarrow H_2 + NO_2$	HMN	–	✓
$H_2^+ + NO_3^- \rightarrow H_2 + NO_3$	HMN	–	✓
$H_2^+ + O_2^- \rightarrow H_2 + O_2$	HMN	–	✓
$H_2^+ + O_3^- \rightarrow H_2 + O_3$	HMN	–	✓
$H_2^+ + O_4^- \rightarrow H_2 + O_2 + O_2$	HDN	–	✓
$H_2^+ + HBr \rightarrow H_2 + HBr^+$	HCX	–	✓
$H_2^+ + Br_2 \rightarrow H_2 + Br_2^+$	HCX	–	✓
$H_2^+ + Br^- \rightarrow Br + H_2$	HMN	–	✓
$H_2^+ + H \rightarrow H_2 + H^+$	HCX	–	✓
$H_2 + H_2^+ \rightarrow H + H_3^+$	HIR	–	✓
$H_2^+ + NH \rightarrow H_2 + NH^+$	HCX	–	✓
$H_2^+ + NH \rightarrow H + NH_2^+$	HIR	–	✓

Dark discharge {Nesamostatný výboj in Czech}

Independent source of charged particle needed.

Source of electrons:

- Cosmic rays
- Ultra-violet light – ionization, photo-detachment
- Radioactive decay (up to the 3 km above Earth surface typically dominant)

At typical atmosphere conditions hundreds – thousands ions in cubic centimeter.

Now we will talk mostly about DC discharges at lower pressures.

V-A characteristic

Only Radon

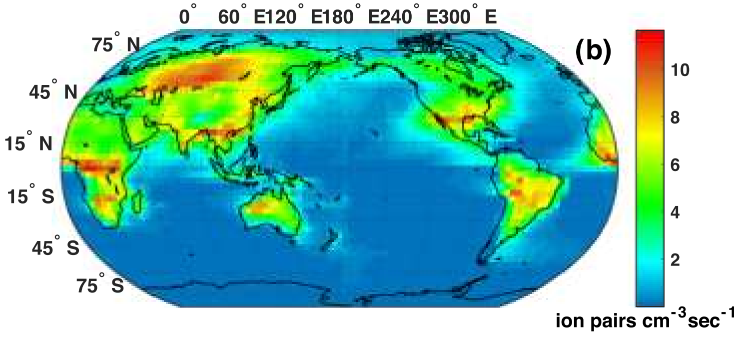


Figure 1. Global map of the modeled Rn-222 mass mixing ratio (panel a) and the corresponding simulated ionization rates (panel b) in the lower model layer for June 2005.

Golubenko K. et al. *Geophys. Res. Lett.* 47 (2020) e2020GL088619
doi: 10.1029/2020GL088619

Townsend avalanche

$$\frac{dn_e}{dx} = \bar{\alpha} n_e \quad \Rightarrow \quad n_e(x) = n_e(0)\exp(\bar{\alpha} x)$$

The first
Townsend coefficient

$$\bar{\alpha} = \begin{pmatrix}\text{ionization}\\ \text{by electron}\end{pmatrix} - \begin{pmatrix}\text{electron}\\ \text{attachment}\end{pmatrix} - \cdots$$

$$\bar{\alpha} = \frac{f_{ion}}{w_e} = \frac{N_\mathrm{n}\langle v_e \sigma\rangle}{w_e} = \frac{N_\mathrm{n}\langle v_e \sigma_i\rangle}{\mu_e E} = \frac{1}{\mu_e}\frac{k_i\left({}^{E}/_{N_\mathrm{n}}\right)}{{}^{E}/_{N_\mathrm{n}}}$$

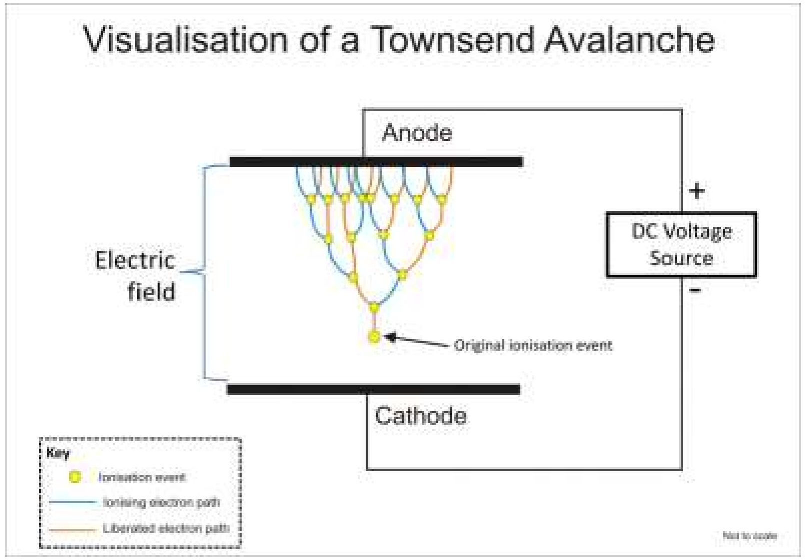
v_e electron velocity
w_e electron drift velocity

$$\frac{\bar{\alpha}}{N_\mathrm{n}} = \mathrm{F}\left({}^{E}/_{N_\mathrm{n}}\right) \qquad \frac{\bar{\alpha}}{p} = \mathrm{F}\left({}^{E}/_{p}\right)$$

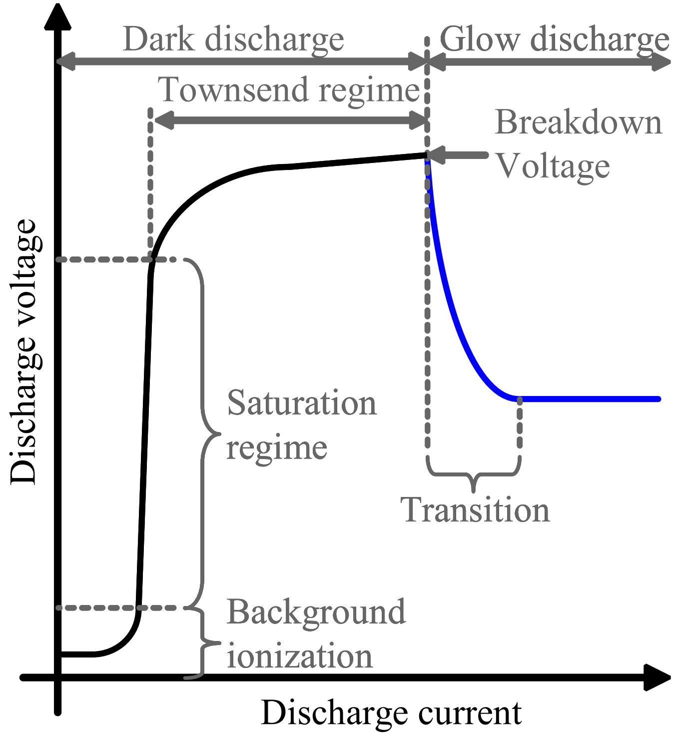
Townsend unit

$1\ \mathrm{Td} = 10^{-17}\ \mathrm{V\,cm^2} = 10^{-21}\ \mathrm{V\,m^2}$

$\mathrm{V\,cm^{-1}\,Pa^{-1}}$



Credit: *Townsend discharge.* (2023, September 21). In Wikipedia.



Granda-Gutiérrez E. E. et al. Proceedings of the 25th IASTED (2006)

Corona discharge

It starts in the high potential gradient that usually occurs at the sharp tips of the electrodes.
single-electrode discharge

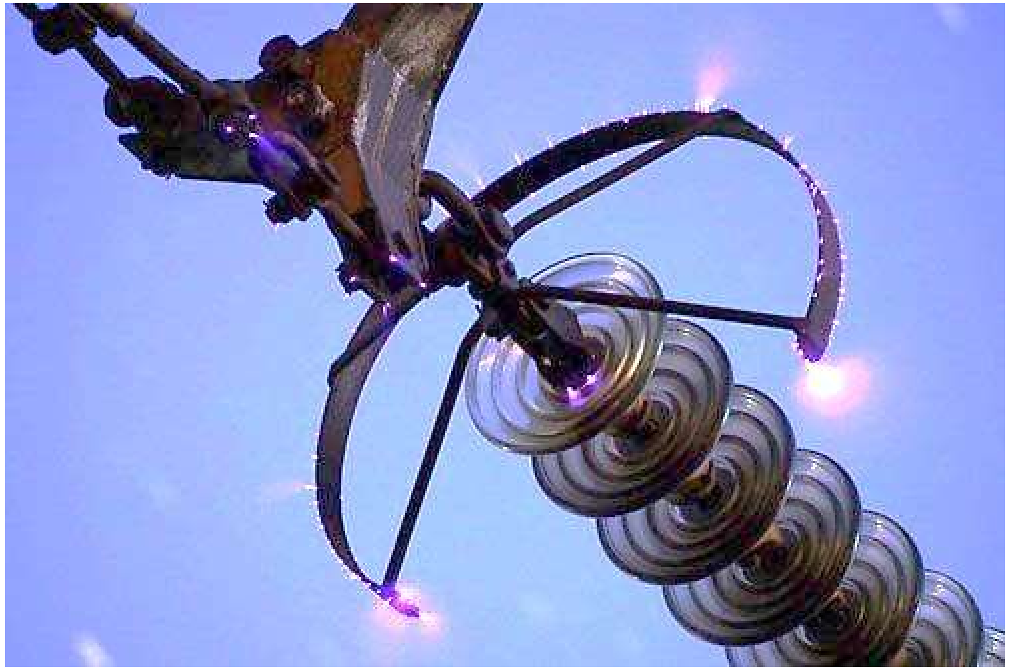
The dielectric strength of the air atmosphere is approximately 3 kV mm^{-1}.

Ionization in electron avalanches and by light from recombination. The expansion of the virtual electrode interrupts the discharge.

Positive corona (anode)
short path of electrons near electrode ⇒ high energy, UV light, homogenous, produce positive ions

Negative corona (cathode)
long electron avalanches at low energy, non-uniform, produce negative ions (ozone)

St. Elmo's fire
{Elijášův oheň in Czech}



Corona ring

Credit: PowerWright Technologies, Inc.

Streamer discharge

Streamers start like a Townsend avalanche.

The density of the avalanche space charge produces an electric field comparable to the external field.

In ambient air

Meek criterion $\bar{\alpha}(E) \cdot d \approx 18$

$$\int_L \bar{\alpha}\big(E(s)\big) \cdot \mathrm{d}s \approx 18$$

Avalanche-to-Streamer transition

It leads to filaments (streamers) formations

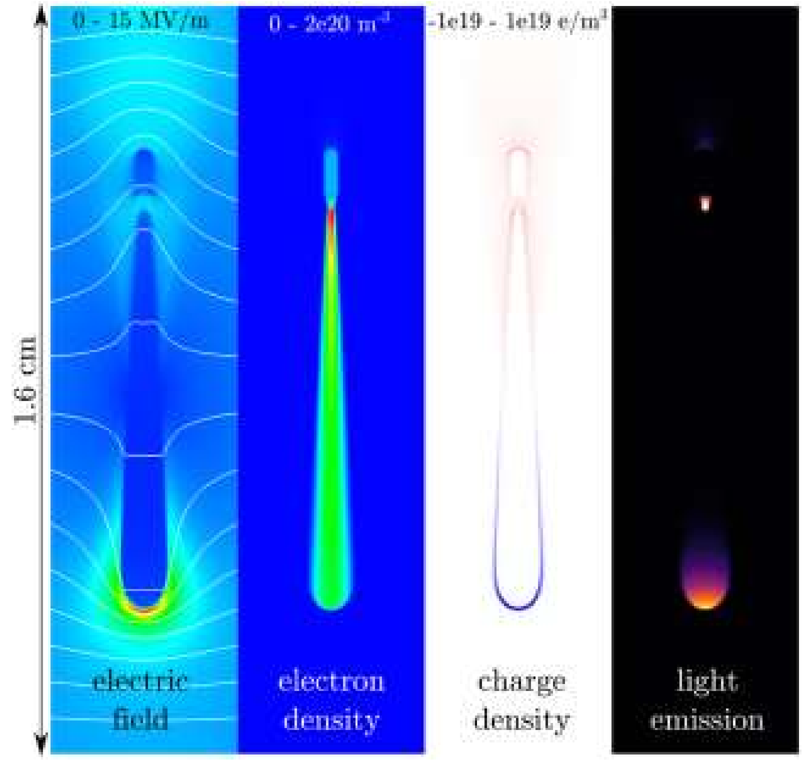
High space charge ⇒
filaments with ionization front

Called also “Filamentary discharge”

Electric field strength $E > E_{\text{critical}}$

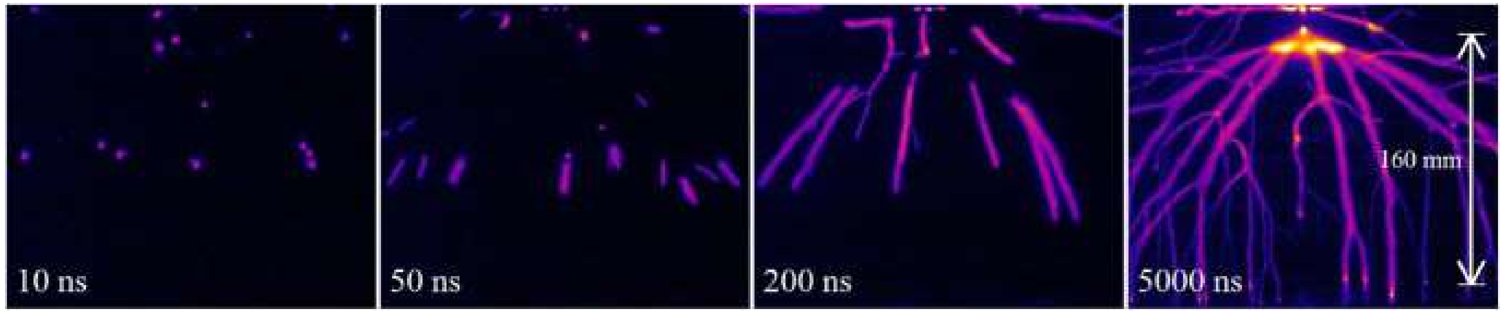
Drifts of an avalanche center $d = \mu_e E t$

$$\exp[\bar{\alpha}(E) \cdot d]$$

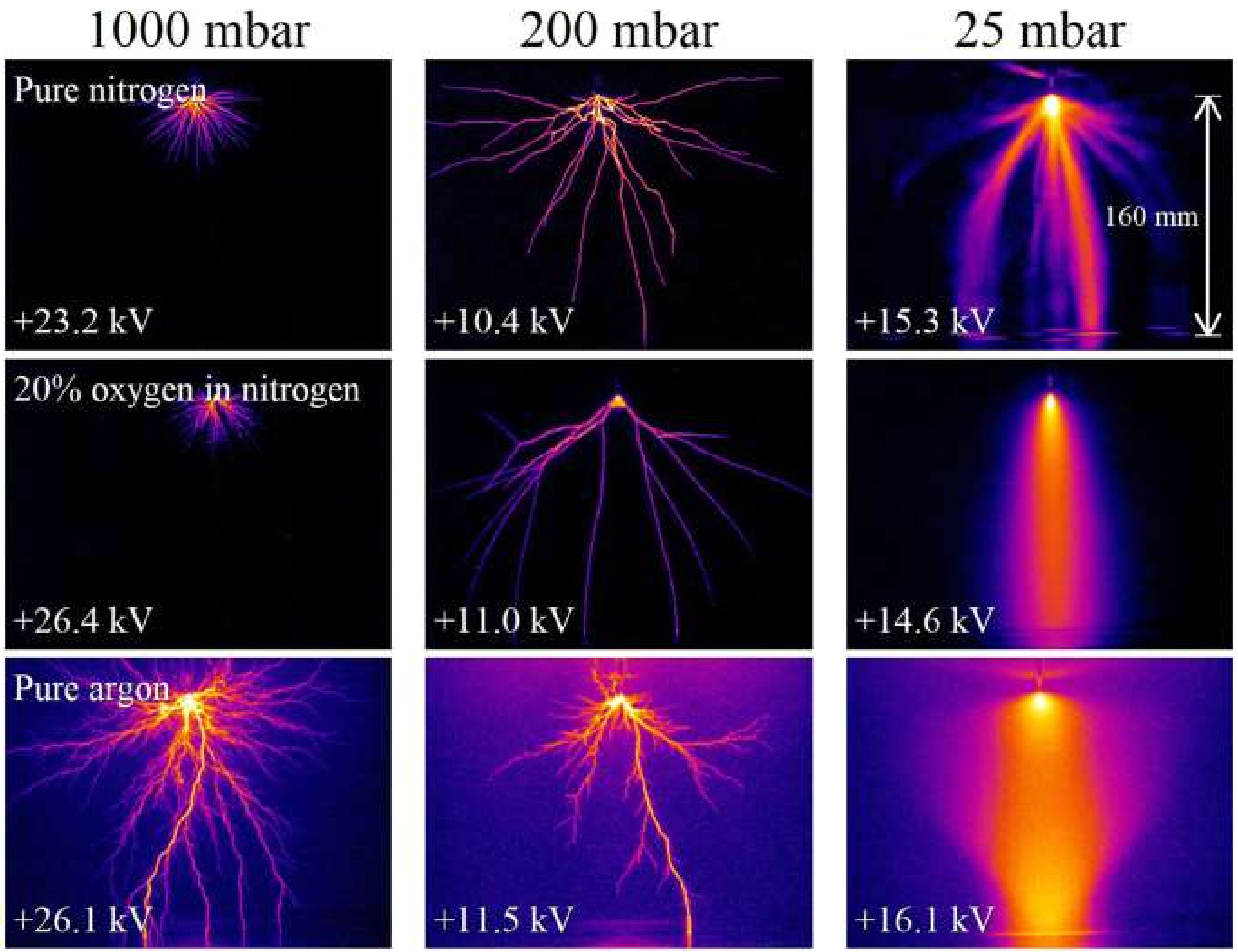


Nijdam S. et al. *Plasma Sources Sci. Technol.* 29 (2020) 103001
doi: 10.1088/1361-6595/abaa05

Streamers positive



Air, 20 kPa, 25 kV



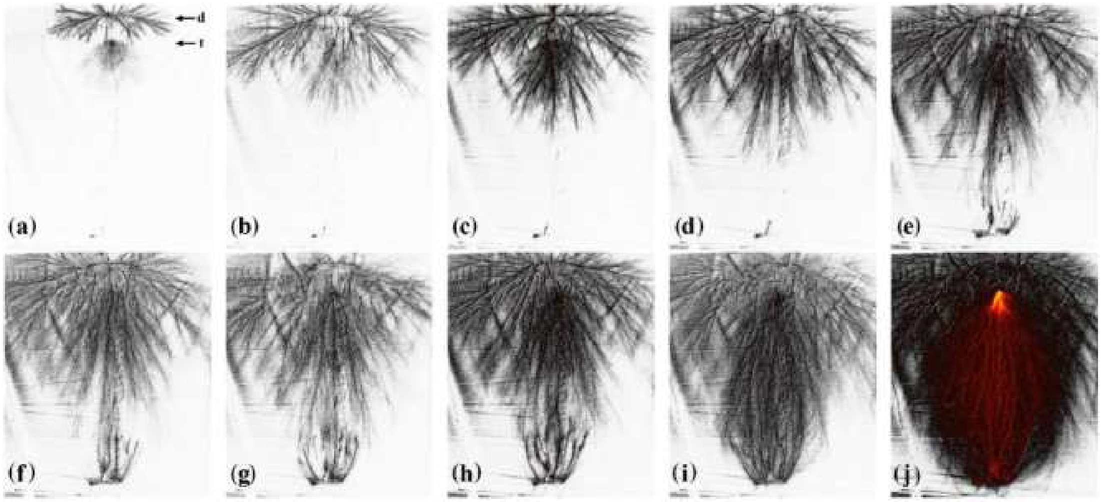
exposure times
2 – 6 µs

Nijdam S. et al. *Plasma Sources Sci. Technol.* 29 (2020) 103001
doi: 10.1088/1361-6595/abaa05

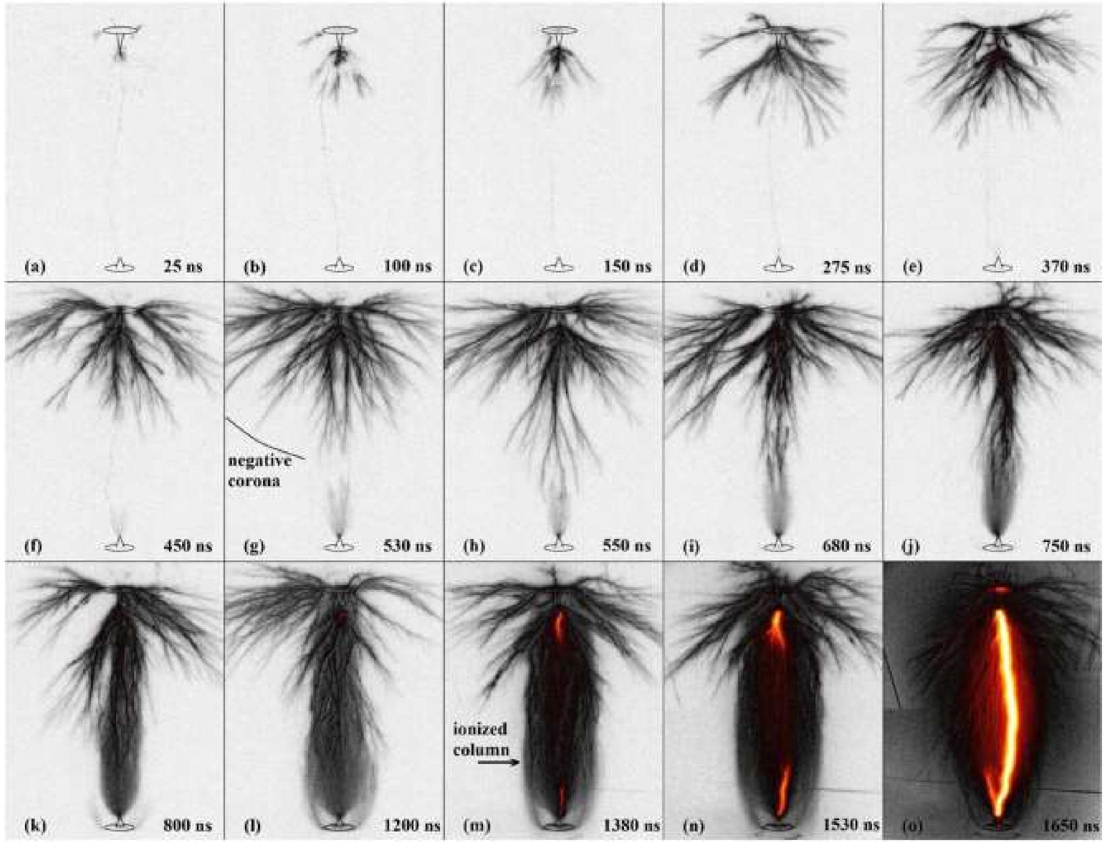
Streamers

Formation of conductive channel
between electrodes
⇒
Spark

Positive



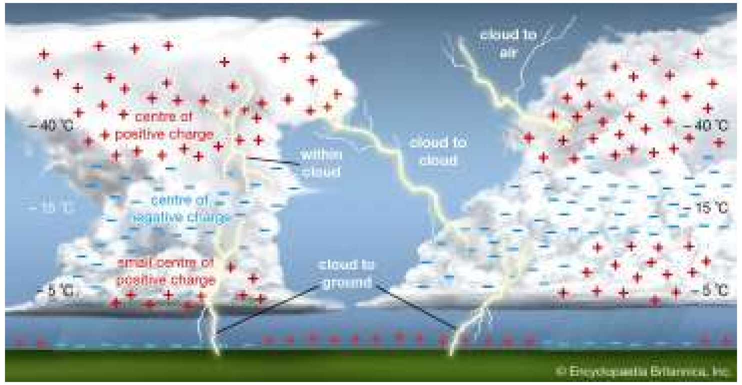
Negative



Kochkin P. O. et al. *J. Phys. D: Appl. Phys.* 45 (2012) 425202
DOI 10.1088/0022-3727/45/42/425202

Lightning in Earth atmosphere

Streamer-to-leader transition
at least 300–500 kV m^{-1}



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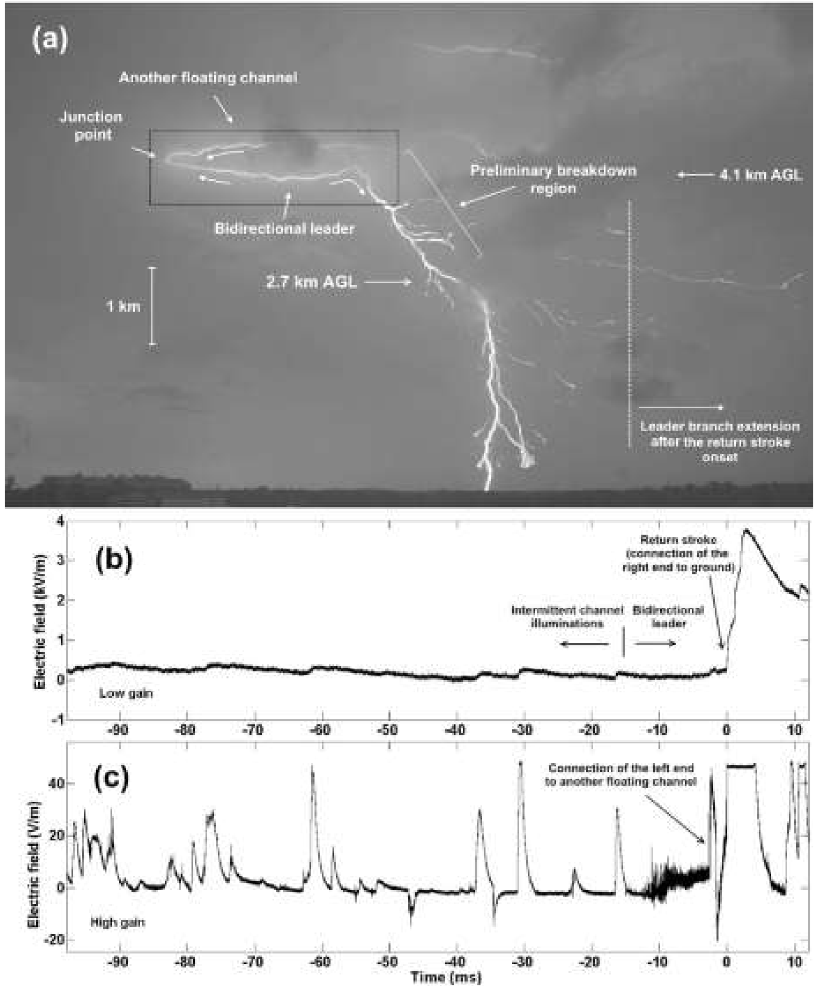
Cloud-to-Ground
Negative Flash

Stepped leader develops downward
in steps typically about 50 meters in length. ≈ 100 km s^{-1}
Close to the ground, it connects with upward streamer.

A conductive path is formed
that balances the charges and creates a flash. ≈ 100 000 km s^{-1}

The median peak current during a fist strike is 30 kA.
later strikes ≈ 10 kA



Tran M. D. & Rakov V. A. *Scientific Reports* 6 (2016) 39521
doi: 10.1038/srep39521

Townsend mechanism

Each primary electron generated near a cathode produces positive ions $i_0 \exp(\bar{\alpha} d) - i_0$

Ions produce electrons from the cathode due to secondary electron emission $\epsilon_i \, i_0 [\exp(\bar{\alpha} d) - 1]$

Townsend second coefficient ϵ_i (0.01 – 0.1)

$$i_{\text{cath}} = i_0 + \epsilon_i \, i_{\text{cath}} [\exp(\bar{\alpha} d) - 1]$$

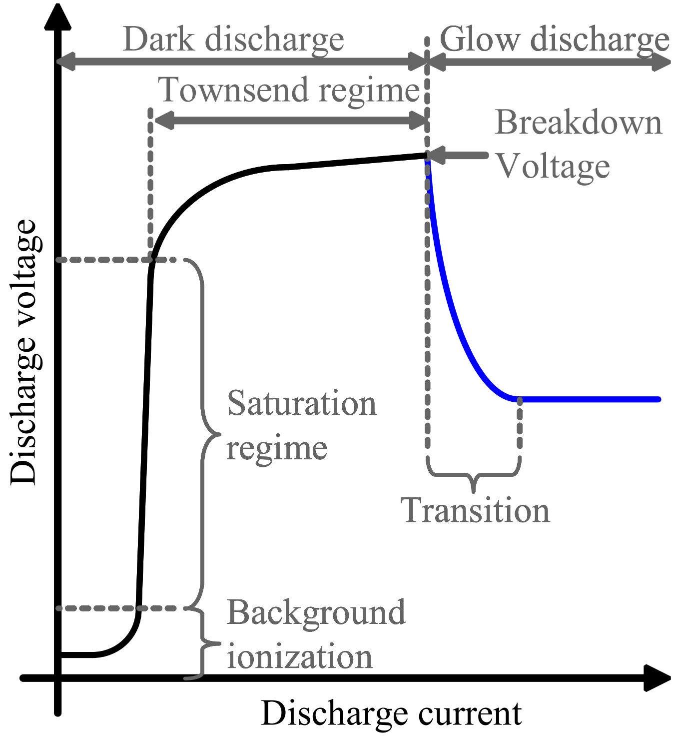
$$\Rightarrow \frac{i_0}{i_{\text{cath}}} = 1 - \epsilon_i \, [\exp(\bar{\alpha} d) - 1]$$

$$\frac{i}{i_0} = \frac{i_{\text{cath}}}{i_0} \exp(\bar{\alpha} d) = \frac{\exp(\bar{\alpha} d)}{1 - \epsilon_i \, [\exp(\bar{\alpha} d) - 1]}$$

Independent discharge

Townsend breakdown

$$1 - \epsilon_i \, [\exp(\bar{\alpha} d) - 1] \leq 0 \quad \Rightarrow \quad \bar{\alpha} d \geq \ln(1 + {\epsilon_i}^{-1})$$



Granda-Gutiérrez E. E. et al. Proceedings of the 25th IASTED (2006)

Townsend mechanism

$$\frac{\bar{\alpha}}{p} = \mathrm{F}\left(\frac{E}{p}\right) \qquad \frac{\bar{\alpha}}{p} = A \exp\left(-\frac{B}{E/p}\right)$$

$$\bar{\alpha} d = pdA \exp\left(-\frac{B}{E/p}\right) = pdA \exp\left(-\frac{Bpd}{U_\mathrm{B}}\right) \geq \ln(1 + {\epsilon_i}^{-1})$$

$$U_\mathrm{B} = \frac{Bpd}{\ln\left[Apd/\ln(1 + {\epsilon_i}^{-1})\right]} = U_\mathrm{B}(pd)$$

$\frac{\mathrm{d}U_\mathrm{B}}{\mathrm{d}(pd)} = 0$ position of minimum

$$U_{\mathrm{B,\,min}} = \frac{\mathrm{e}B}{A}\ln(1 + {\epsilon_i}^{-1})$$

e … Euler number

$$(pd)_\mathrm{min} = \frac{\mathrm{e}}{A}\ln(1 + {\epsilon_i}^{-1})$$

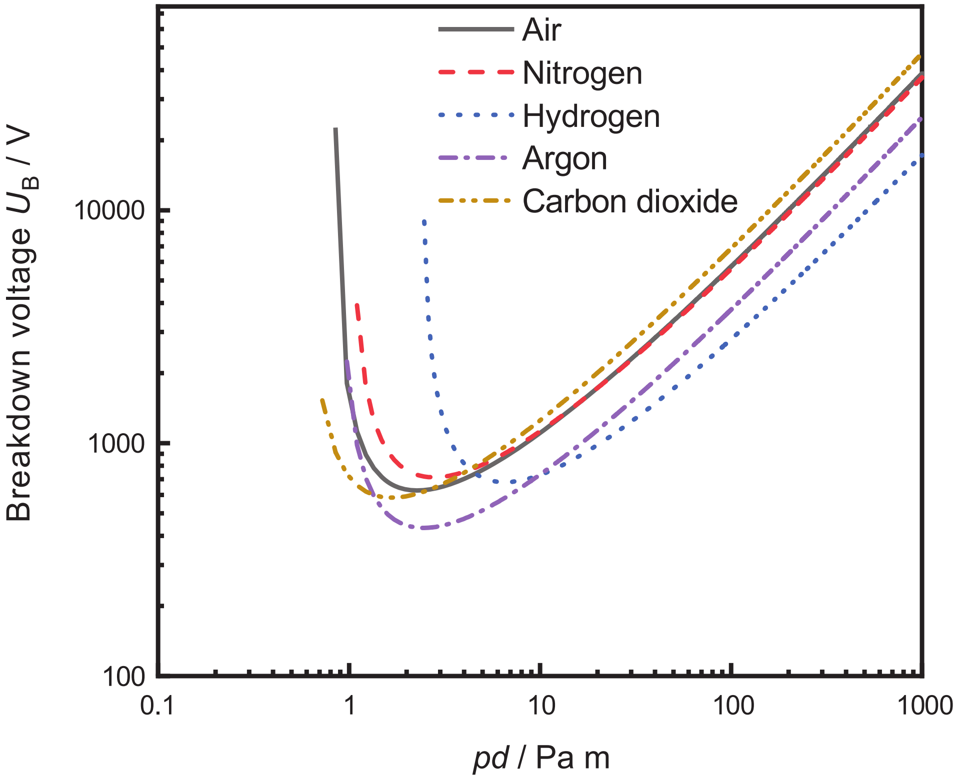
A, *B* parameters for different gases

Pressure *p*

Breakdown potential over a distance *d*

$$U_\mathrm{B} = E \cdot d$$

Paschen's law



Ollegott K. et al. *Chem. Ing. Tech.* 92 2020 1.
doi: 10.1002/cite.202000075