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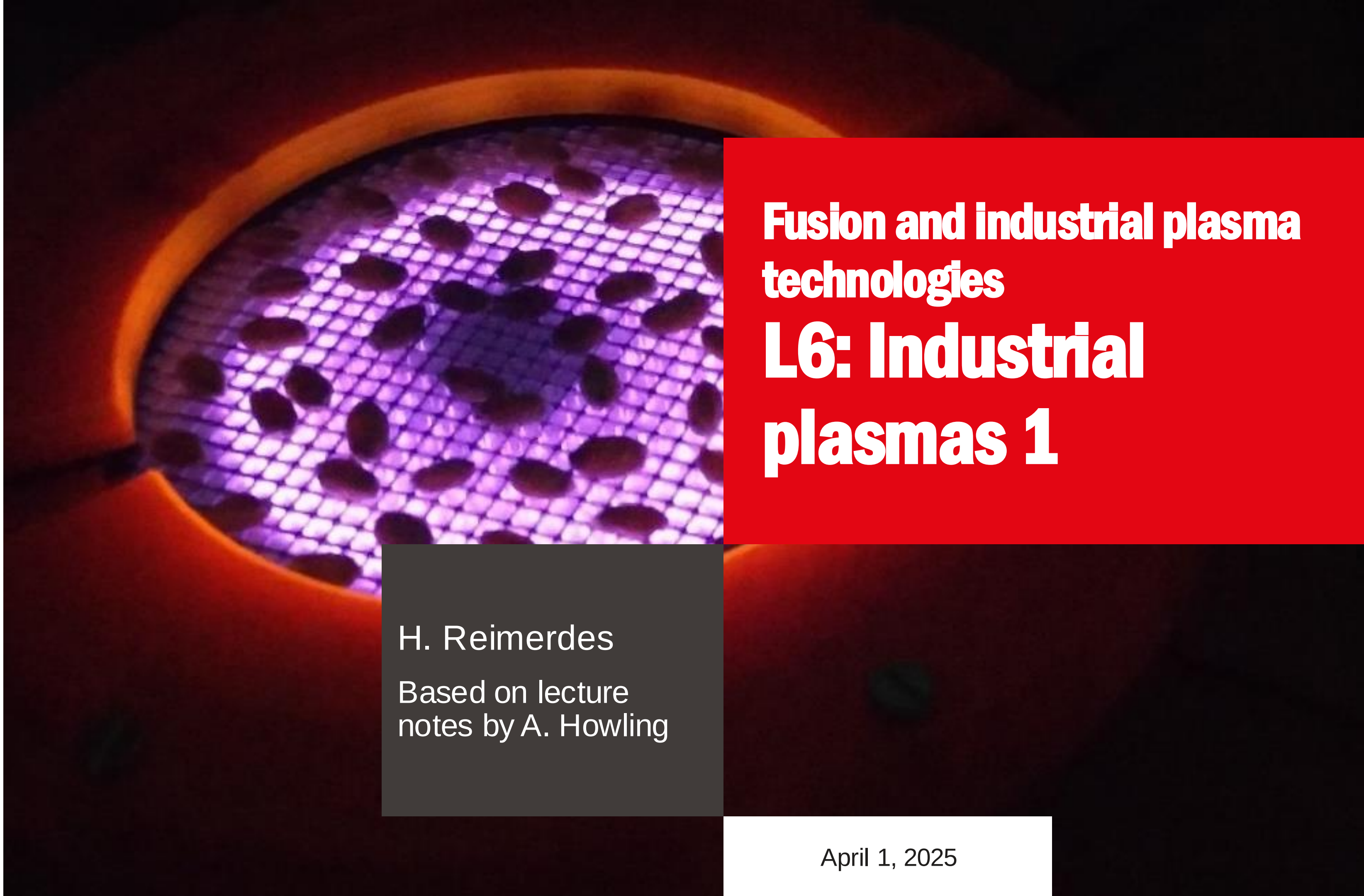


Fusion and industrial plasma technologies

L6: Industrial plasmas 1

H. Reimerdes

Based on lecture notes by A. Howling

April 1, 2025

Swiss Plasma Center

Outline

1. Introduction to basic industrial plasmas
   - Plasma medicine
2. Breakdown and Paschen's law
   - Communication satellite

This week

3. Sheath and plasma etching
   - Microelectronics
4. Plasma with insulating electrodes
   - Large area displays/solar cells

Next week

Material

- See also EPFL MOOC "Plasma physics: Applications" #5a-g
  - https://courses.edx.org/courses/course-v1:EPFLx+PlasmaApplicationX+1T_2018
- Braithwaite, "Introduction to gas discharges", *Plasma Sources Sci. Technol.* **9** (2000) 517

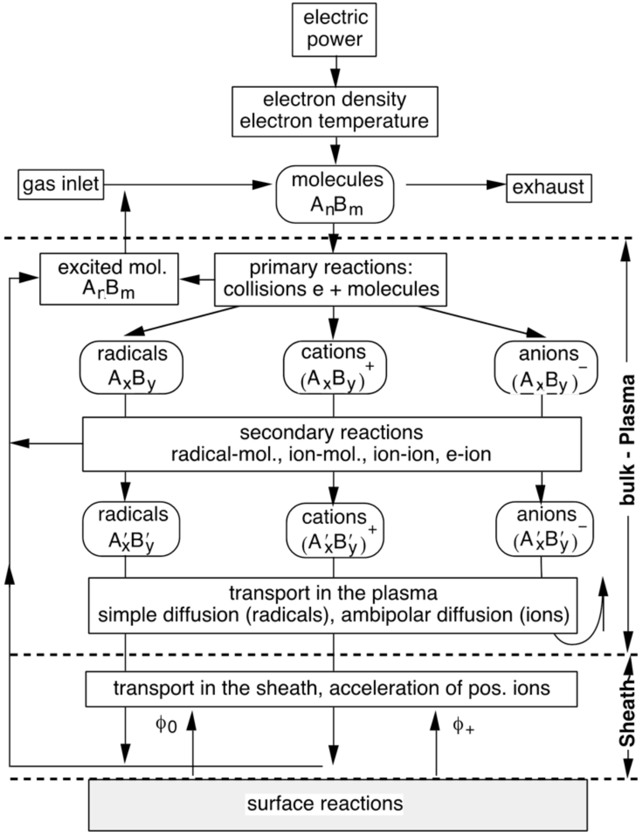
Industrial plasma applications

- Microelectronics
  - LED/GaN
  - Photovoltaic solar cell panels (e.g. Meyer Burger)
- Superconducting layers (e.g. CERN)
- Food packaging (e.g. TetraPak)
- Refractory/hard/decorative coatings
- Surface activation (implants, architectural glass, e.g. Comelec)
- Powder/grain treatment
- Space industry and aeronautics (e.g. Ruag Space)
- Electrical discharge machining
- Combustion, waste treatment (e.g. DAPHNE Technology)
- Medical
  - Sterilisation
  - Wound treatment
  - Dental treatment
  - Cancer treatment

Why plasma chemistry is difficult

Compare with fusion plasmas

- Higher pressure (order of mbar) of neutrals
- Lower degree of ionisation ~10^{-6} to 10^{-3}
- Collisional damping, no waves
- Often no magnetic field, no MHD



Next week

EPFL

Different types of reactions

Gas phase reactions (homogeneous) involving electrons	
Ionisation	$e^- + A \rightarrow A^+ + 2e^-$ $e^- + AB \rightarrow AB^+ + 2e^-$
Dissociation (fragmentation)	$e^- + AB \rightarrow A + B + e^-$
Dissociative attachment	$e^- + AB \rightarrow A^- + B$

Surface reactions (heterogeneous)	
Recombination	$e^- + A^+ + \mathrm{srfc} \rightarrow A$
Association	$A + B + \mathrm{srfc} \rightarrow AB$
Secondary emission	$A^+ + \mathrm{srfc} \rightarrow A + e^-$ (from srfc)
Sputtering (dry etching)	$A^+ + \mathrm{srfc}[C] \rightarrow C$
Deposition	$A + \mathrm{srfc}[C] \rightarrow \mathrm{srfc}[AC]$
Etching (wet)	$A + \mathrm{srfc}[C] \rightarrow AC$

- Transport of species to surface
  - Neutrals: Diffusion of species A with $-D_A \nabla n_A$
  - Ions: Ion flux across sheath (see next lecture) with $n^+ v_{\mathrm{Bohm}}$

Example: Simple oxygen plasma

- Some binary reactions:

Number	Reaction	Rate Constant (cm^3/s)
Reactions among e, O_2, O_2^+, and O^-		
1	$e + O_2$ momentum transfer	$4.7E{-}8T_e^{0.5}$
2	$e + O_2 \rightarrow O^- + O$	$8.8E{-}11 \exp(-4.4/T_e)$
3	$e + O_2 \rightarrow 2O + e$	$4.2E{-}9 \exp(-5.6/T_e)$
4	$e + O_2 \rightarrow O_2^+ + 2e$	$9.0E{-}10T_e^{0.5} \exp(-12.6/T_e)$
5	$e + O^- \rightarrow O + 2e$	$2.0E{-}7 \exp(-5.5/T_e)$
6	$e + O_2^+ \rightarrow 2O$	$5.2E{-}9/T_e$
7	$O^- + O_2^+ \rightarrow O + O_2$	$(0.96, 2)E{-}7(300/T)^{0.5}$
8	$O^- + O \rightarrow O_2 + e$	$(1.4, 5)E{-}10$
9	$O^- + O_2^+ \rightarrow 3O$	$1E{-}7$
Addition of O^+		
10	$e + O_2 \rightarrow O^- + O^+ + e$	$7.1E{-}11T_e^{0.5} \exp(-17/T_e)$
11	$e + O_2 \rightarrow O + O^+ + 2e$	$5.3E{-}10T_e^{0.9} \exp(-20/T_e)$
12	$e + O \rightarrow O^+ + 2e$	$9.0E{-}9T_e^{0.7} \exp(-13.6/T_e)$
13	$O^- + O^+ \rightarrow 2O$	$(2.7, 2)E{-}7(300/T)^{0.5}$
14	$O^+ + O_2 \rightarrow O + O_2^+$	$2.0E{-}11(300/T)^{0.5}$
Addition of metastable $O_2^*(^1\Delta_g)$; see note f below		
15	$e + O_2 \rightarrow O_2^* + e$	$1.7E{-}9 \exp(-3.1/T_e)$
16	$e + O_2^* \rightarrow e + O_2$	$5.6E{-}9 \exp(-2.2/T_e)$
17	$O_2^* + O_2 \rightarrow 2O_2$	$2.2E{-}18(T/300)^{0.8}$
18	$O_2^* + O \rightarrow O_2 + O$	$(1.0, 7)E{-}16$
Addition of metastable $O(^1D)$		
19	$e + O_2 \rightarrow O + O^* + e$	$5.0E{-}8 \exp(-8.4/T_e)$
20	$e + O \rightarrow O^* + e$	$4.2E{-}9 \exp(-2.25/T_e)$
21	$e + O^* \rightarrow e + O$	$8E{-}9$
22	$e + O^* \rightarrow O^+ + 2e$	$9.0E{-}9T_e^{0.7} \exp(-11.6/T_e)$
23	$O^* + O \rightarrow 2O$	$8.0E{-}12$
24	$O^* + O_2 \rightarrow O + O_2$	$(6.4, 7.0)E{-}12 \exp(67/T)$
25	$O^* + O_2 \rightarrow O + O_2^*$	$1.0E{-}12$
Addition of selected reactions for O_2^- and O_3		
26	$O^- + O_2 \rightarrow O_3 + e$	$5E{-}15$
27	$e + O_3 \rightarrow O_2^- + O$	$1E{-}9$
28	$O^- + O_2^* \rightarrow O_3 + e$	$3E{-}10$
29	$O^- + O_2^* \rightarrow O_2^- + O$	$1E{-}10$
30	$O_2^- + O_2^+ \rightarrow 2O_2$	$2E{-}7(300/T)^{0.5}$
31	$O_2^- + O^+ \rightarrow O_2 + O$	$2E{-}7(300/T)^{0.5}$
32	$O_3 + O_2 \rightarrow O_2 + O + O_2$	$7.3E{-}10 \exp(-11400/T)$
33	$O_3 + O \rightarrow 2O_2$	$1.8E{-}11 \exp(-2300/T)$

Elastic collisions (→ Exercise 1)

- Conservation of momentum and energy yields maximum energy transfer from *m* to *M*

$$\delta_{\max} = \frac{4mM}{(m+M)^2}$$

  - For an electron hitting an atom: $m \ll M$ → $\delta_{\max} \sim \frac{4m}{M} \ll 1$
  - For an ion hitting an atom: $m \approx M$ → $\delta_{\max} \sim 1$

Ex. Ar with A=40
$m_{Ar} = 1836 \times 40 \cdot m_e$
→ $\delta_{max} \sim \frac{1}{18000}$

➢ Electrons do not efficiently heat the gas

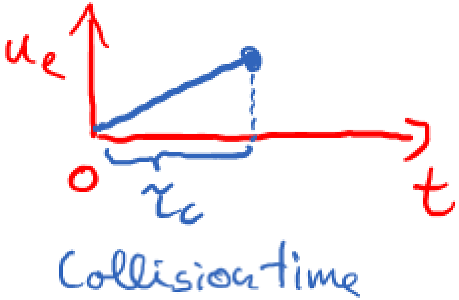
➢ Ions thermalise efficiently with the gas (typically at 'room' temperature)

Heating and electron power balance

- Electrons gain energy from the electric field $\bar{E}$ and transfer it to the gas
  - Average power gain per e: $\text{Electric force} \times \text{electron drift speed}$

$$\bar{P}_{e,\text{gain}} = Ee \cdot u_e = ?$$

Drift velocity



$$a = \frac{F}{m_e} = \frac{q_e E}{m_e}$$

$$u_e^{max} = a \cdot \tau_c$$

$$= \frac{q_e E}{m_e} \cdot \frac{1}{\nu_{e/n}} = \frac{q_e}{m_e \nu_{e/n}} \cdot E$$

Mobility μ_e

Heating and electron power balance

- Electrons gain energy from the electric field $\bar{E}$ and transfer it to the gas
  - Average power gain per e: $\text{Electric force} \times \text{electron drift speed}$

$$\bar{P}_{e,\text{gain}} = Ee \cdot u_e = Ee \cdot \underbrace{\mu_e E}_{u_e} = Ee \cdot \frac{e}{m_e \nu^{e/n}} E = \frac{e^2 E^2}{m_e \nu^{e/n}}$$

  - For an average electron temperature T_e and gas temperature T_{gas} the average energy loss per collision is $\sim \frac{3}{2} \delta e \left(T_e - T_{\text{gas}}\right)$
  - Average power loss per *e*:

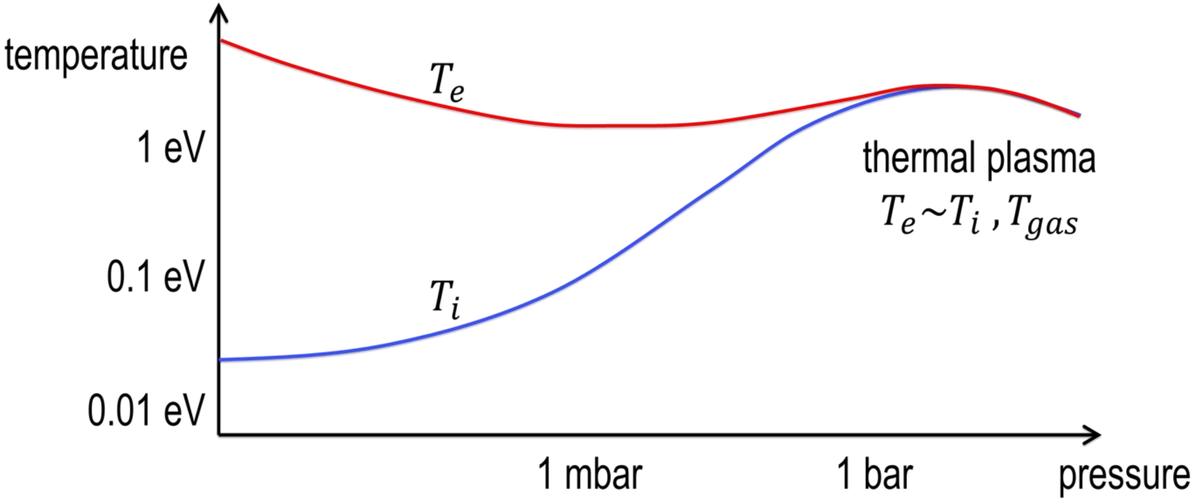
$$\bar{P}_{e,\text{loss}} = \frac{3}{2} \delta e \left(T_e - T_{\text{gas}}\right) \nu^{e/n}$$

- Steady-state

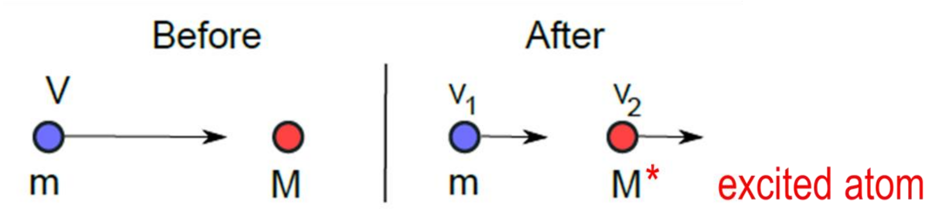
$$\left(T_e - T_{\text{gas}}\right) = \frac{2eE^2}{3\delta m_e (\nu^{e/n})^2} \propto \left(\frac{1}{\text{pressure}}\right)^2$$

Low pressure, non-equilibrium plasma

$$\left(T_e - T_{\text{gas}}\right) = \frac{2eE^2}{3\delta m_e (\nu^{e/n})^2} \propto \left(\frac{1}{\text{pressure}}\right)^2$$



Inelastic collisions (→ Exercise 1)



- Conservation of momentum and energy including internal energy
  - The maximum electron energy transferred to internal energy is $\frac{M}{m+M} \approx 1$
  - The simultaneous fraction of transferred kinetic energy is $\frac{mM}{(m+M)^2} \ll 1$

➢ High energy electrons can modify chemical bonds without heating the gas

Key to industrial plasma processing and medical applications

- Low temperature ($T_e \sim 2eV \approx 23{,}000K$), non-equilibrium plasma ($T_e \gg T_{\mathrm{gas}}$)

➢ High temperature plasma chemistry on low temperature substrates (e.g. glass, plastic, people)

- Rate of chemical reactions

$$k = Ae^{-\frac{E_a}{k_B T}}$$

Arrhenius' equation

+ With activation energy E_A and reaction specific pre-exponential factor A

→ See exercise 2 for numerical values

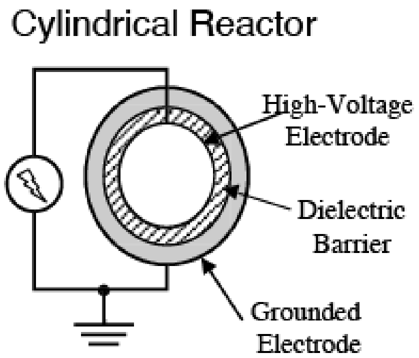
Plasmas in medicine

- Low temperature plasmas can generate reactive species
  - Reactive oxygen species (**ROS**), e.g. peroxides and superoxides
  - Reactive nitrogen species (**RNS**)
- Low temperature plasma emit in the UV
- Effects on tissue and cells
  - Sterilisation, decontamination, blood coagulation
- Application
  - Treatment of skin, wounds and ulcers
  - Cancer treatment
  - Dental care

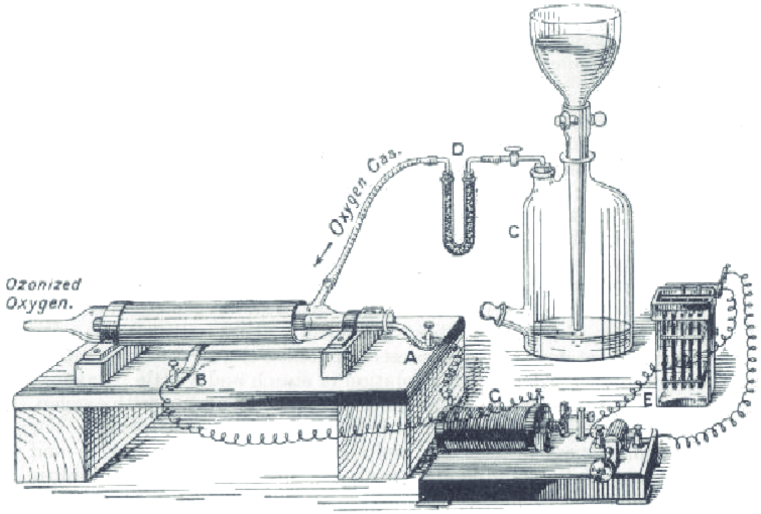
! Plasma-medical mechanisms not fully understood

Plasma sources for medical applications

- **Example:** Dielectric-barrier discharge (DBD) - First use reported by *von Siemens* in 1857, primarily used for ozon production until only very recently



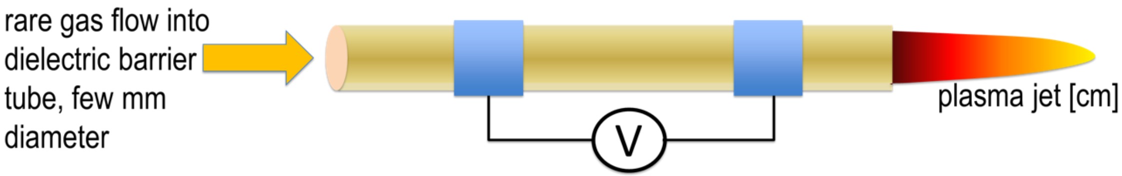
[Wagner, et al., Vacuum 73 (2003)]



  - Suitable for high gas pressure
  - Operated between line frequency and 10MHz

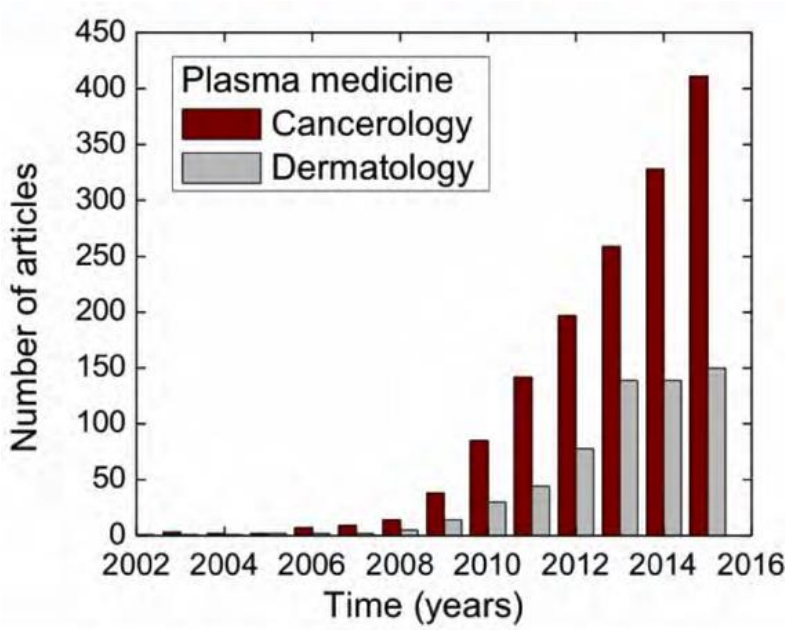
Plasma delivery for medical applications

- Example tool: Low temperature DBD plasma jet in air



Plasmas in medicine

- Complex, but rapidly evolving new field of research



Excursus: units of temperature in plasma physics

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- Statistical mechanics relates the *temperature* of a system in thermal equilibrium to its average *energy*

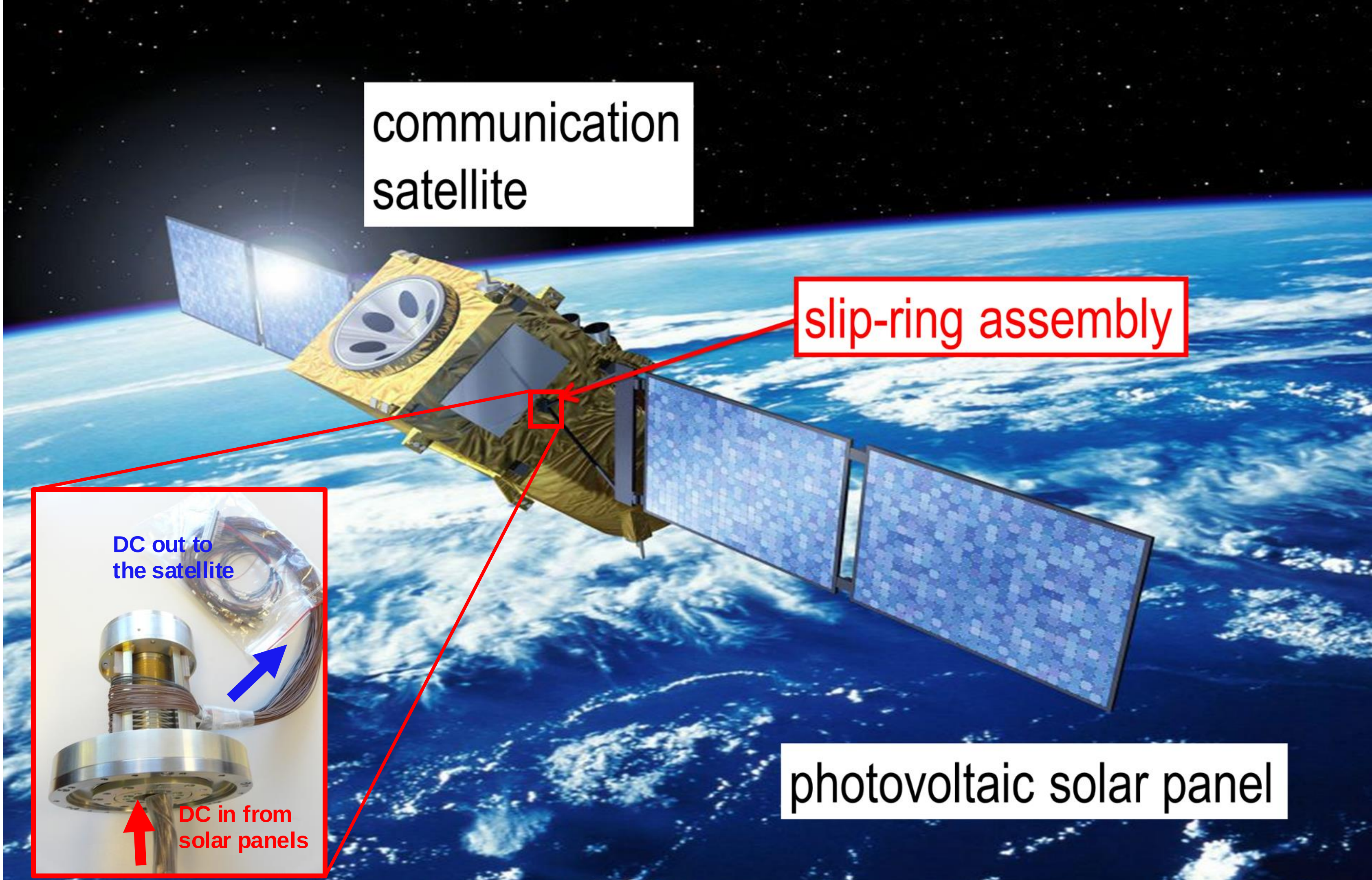
Each degree of freedom of a freely moving particle has, on average, an energy equal to $(k_B T)/2$, where $k_B = 1.38 \times 10^{-23}$J/K is Boltzmann's constant.

- It is common practice in plasma physics to replace large numbers in K or small numbers in J with the potential difference that corresponds to the same energy for an elementary charge -> *electron-volts*
- In industrial applications the 'electron' is often skipped

Summary of ‘Introduction to basic industrial plasmas’

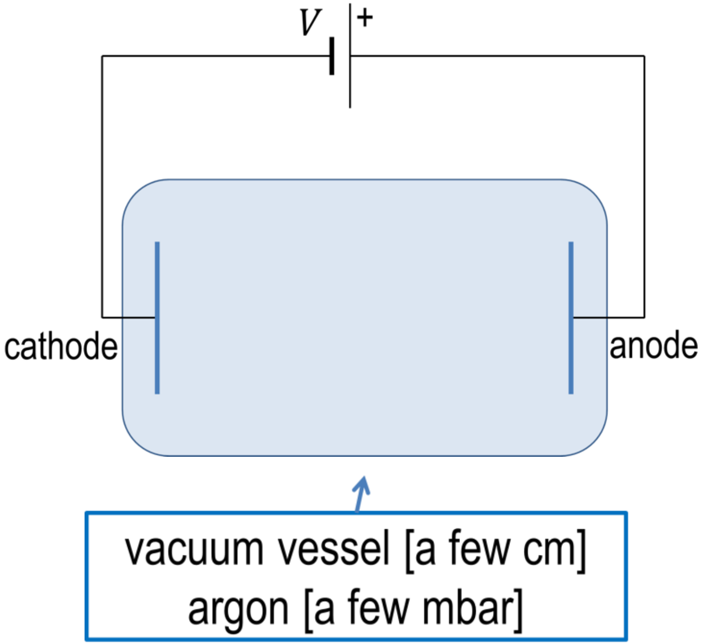
- Low temperature, non-equilibrium plasmas
- Electrons are hotter than ions and gas and facilitate chemical reactions
- Key to industrial plasma processing and medical applications: high temperature plasma chemistry on low temperature substrates

Outline


communication satellite
slip-ring assembly
DC out to the satellite
DC in from solar panels
photovoltaic solar panel

Background ionisation

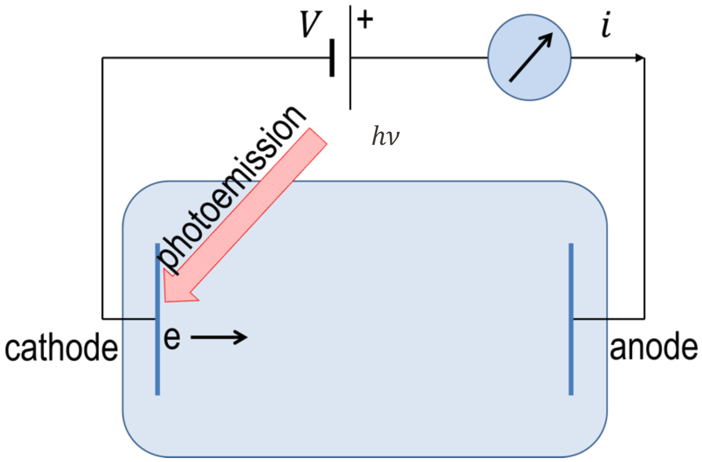
- **Apply a DC voltage between parallel electrodes**
- How does the plasma start?
- Where does the first electron come from?

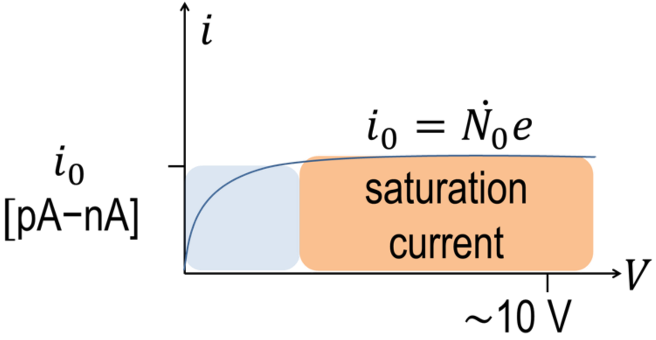


Background ionisation

- Background radiation: cosmic rays, radioactivity
  - Photoemission from electrodes: $h\nu > e\phi$
  - (Photoionisation of gas)

- *Saturation current*: All created charges are collected at the electrodes
- Discharge too weak to be visible
- Depends on external source → not self-sustaining



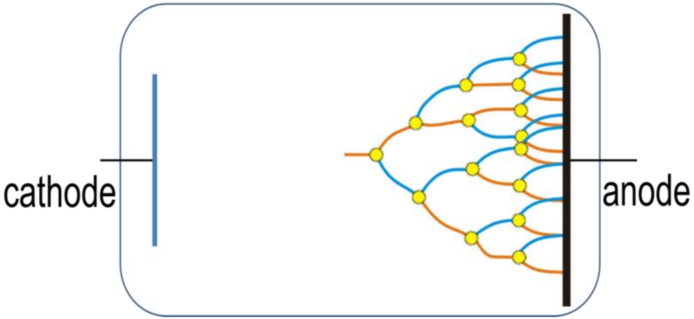


First Townsend coefficient α

- Increase voltage further
  - Ionisation by electron impact creates more electrons

$$e^- + Ar \rightarrow 2e^- + Ar^+$$

  - The discharge current increases above saturation current
  - Each initial electron can create an avalanche of electron-ion pairs

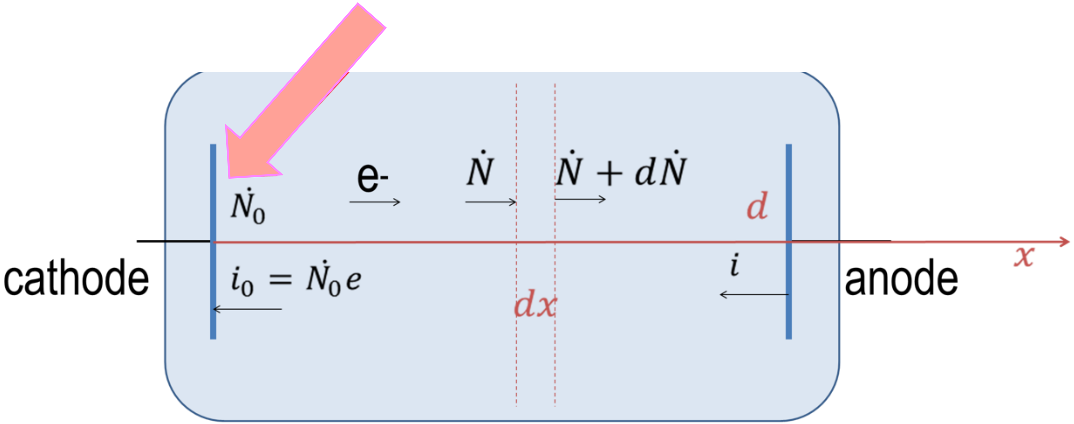


- Introduce *Townsend's first ionisation coefficient*

  α: number of ionising collisions per electron and unit length along E

First Townsend coefficient α

- Evolution of the electron current



By definition of α : $d\dot{N} = \dot{N}\ \alpha\ dx$

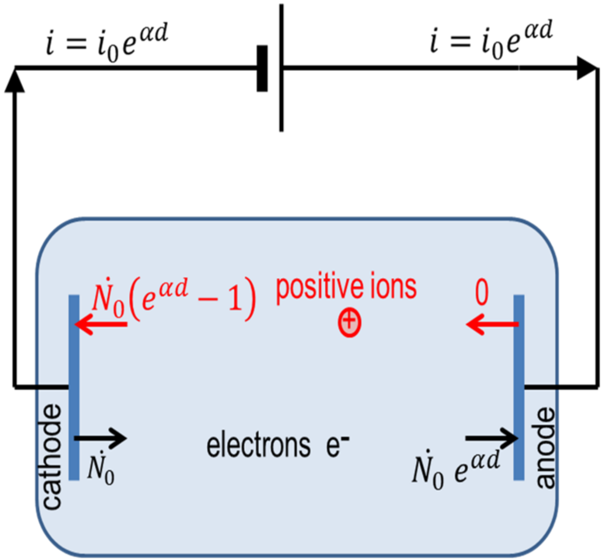
Integrate from cathode to plane at x : $\int_{\dot{N}_0}^{\dot{N}} \frac{d\dot{N}}{\dot{N}} = \int_0^x \alpha\ dx$

If α independent of x: $\dot{N} = \dot{N}_0\ e^{\alpha x}$

Current leaving the anode : $i = \dot{N}_0 e\ e^{\alpha d} = i_0 e^{\alpha d}$ AVALANCHE effect

Townsend discharge

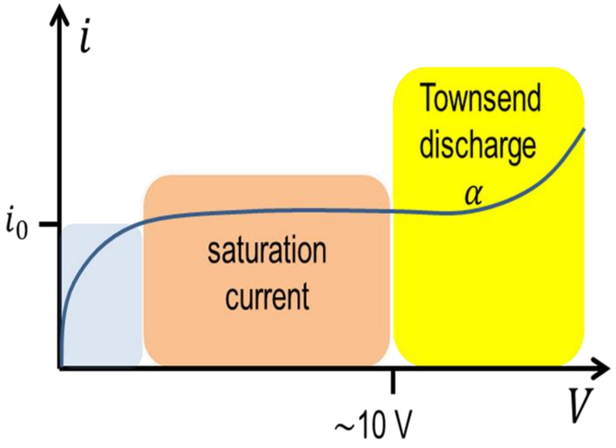
- Continuity of current

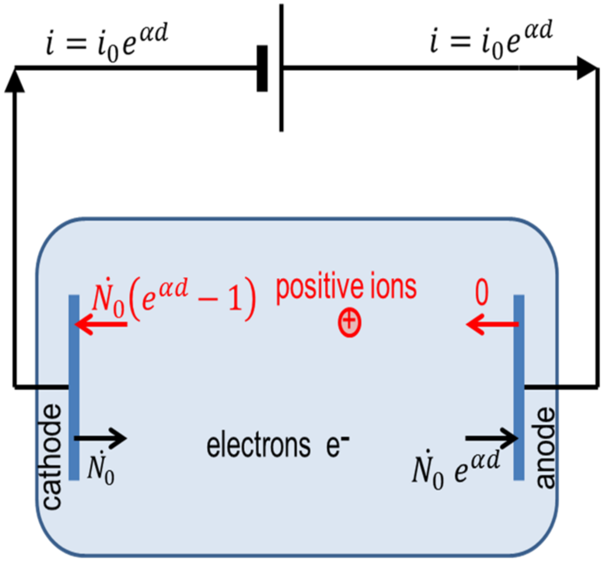


The current crossing any plane is everywhere the same,
$i = i_0 e^{\alpha d}$

Townsend discharge

- Continuity of current





The current crossing any plane is everywhere the same, $i = i_0 e^{\alpha d}$

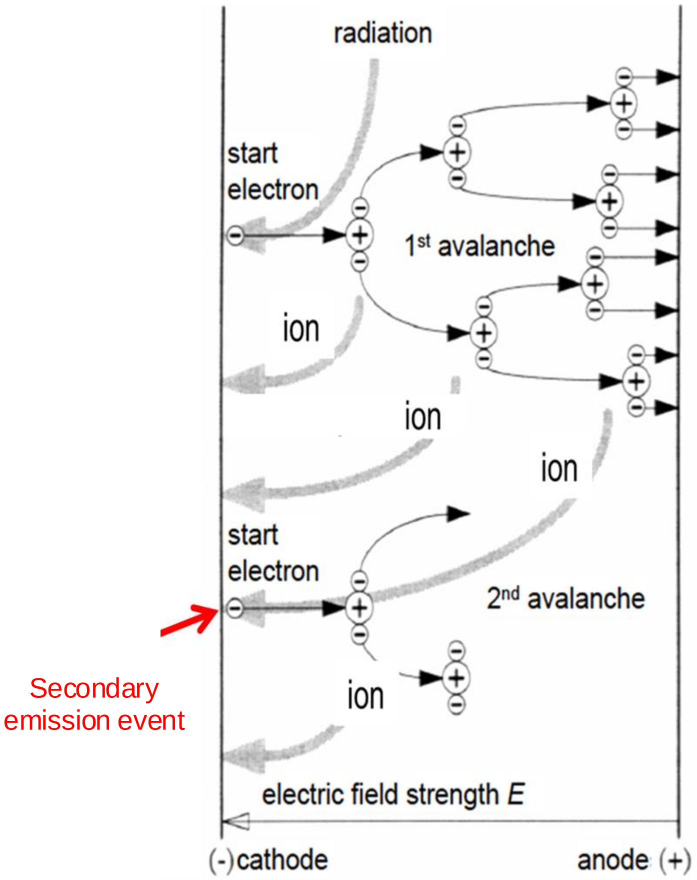
  - Current increases, but depends entirely on an external source → Townsend discharge is not a self-sustained discharge

Second Townsend coefficient γ

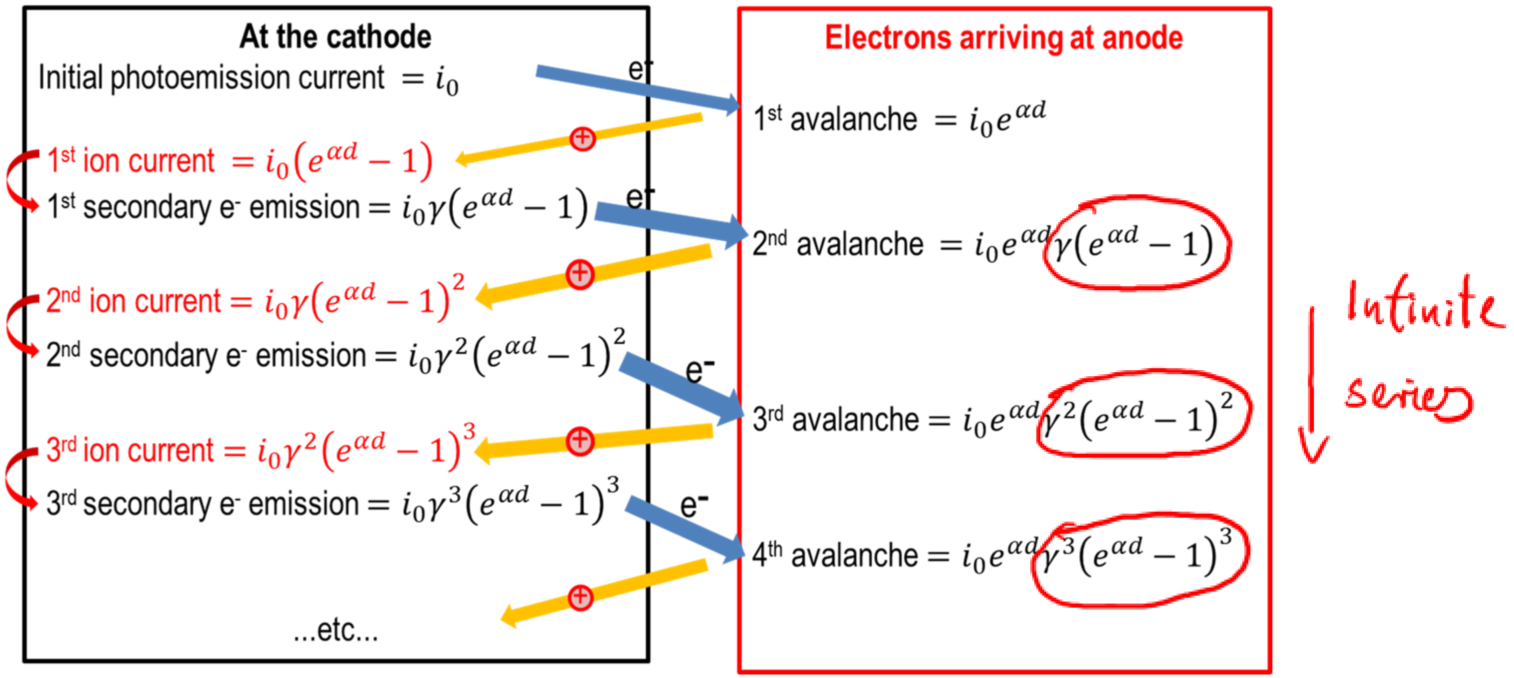
- Current can increase even more strongly due to secondary emission
- *Townsend's second ionisation coefficient*

  γ: number of electrons emitted per incident ion (~10^{-2})

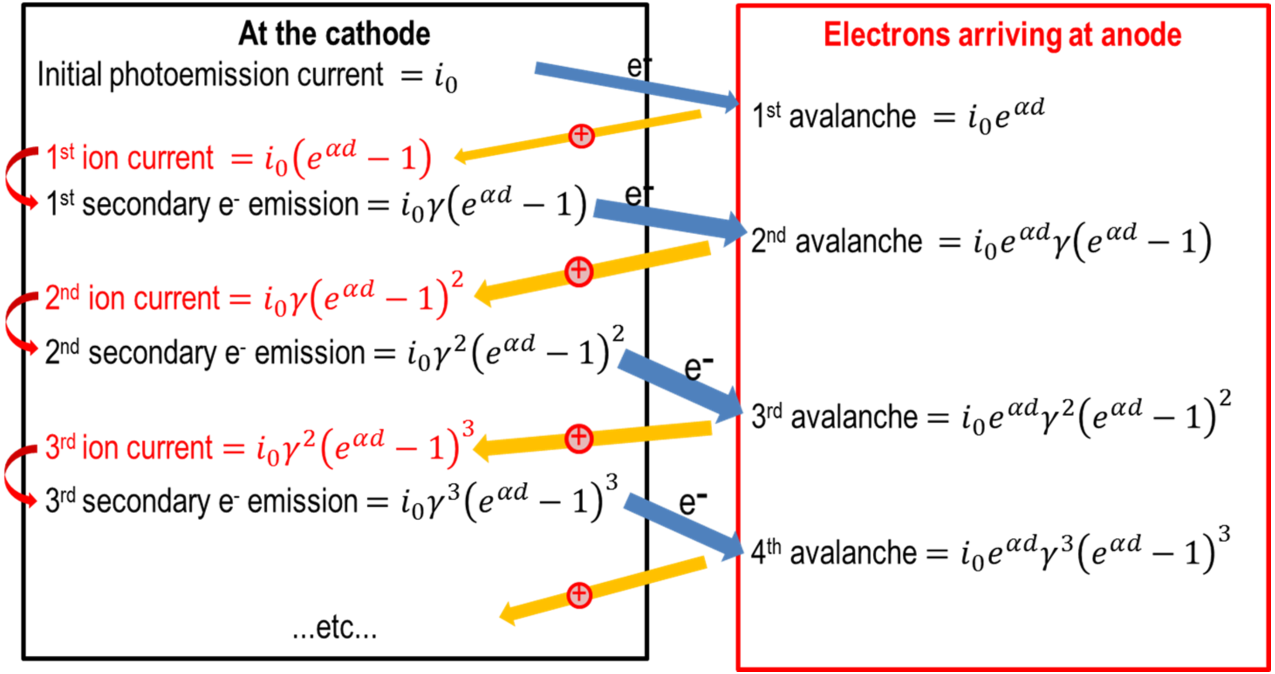
  - Depends on gas type and electrode material (e.g. work function)



Second Townsend coefficient γ



Second Townsend coefficient γ



➢ **Sum of infinite series at anode:** $i = \dfrac{i_0 e^{\alpha d}}{1-\gamma(e^{\alpha d}-1)}$

Breakdown criterion in gases

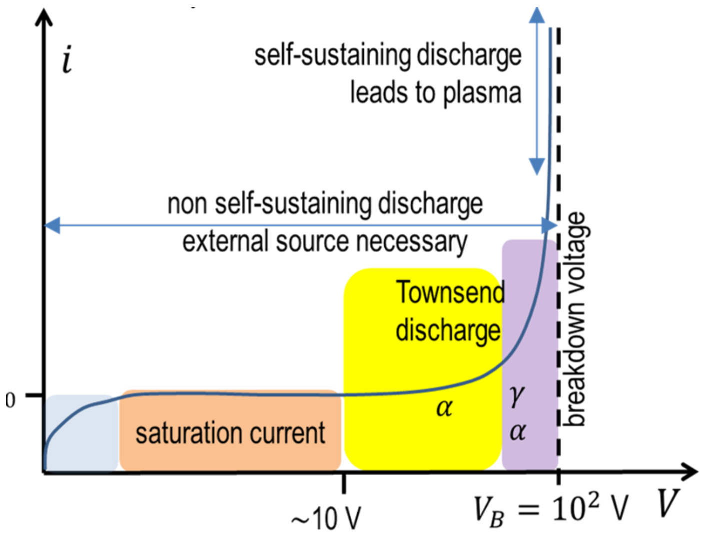
- Current

$$i = \frac{i_0 e^{\alpha d}}{1 - \gamma(e^{\alpha d} - 1)}$$

- *Townsend criterion for breakdown*

$$1 - \gamma\left(e^{\alpha d} - 1\right) = 0$$

$$\Leftrightarrow \boxed{\gamma e^{\alpha d} = \gamma + 1 \approx 1}$$



- The gas 'breaks down' and becomes a self-sustained discharge → independent of external source i_0
  - $\gamma e^{\alpha d}$: number of secondary electrons emitted per primary electron
  - Replace each primary electron with a new secondary electron

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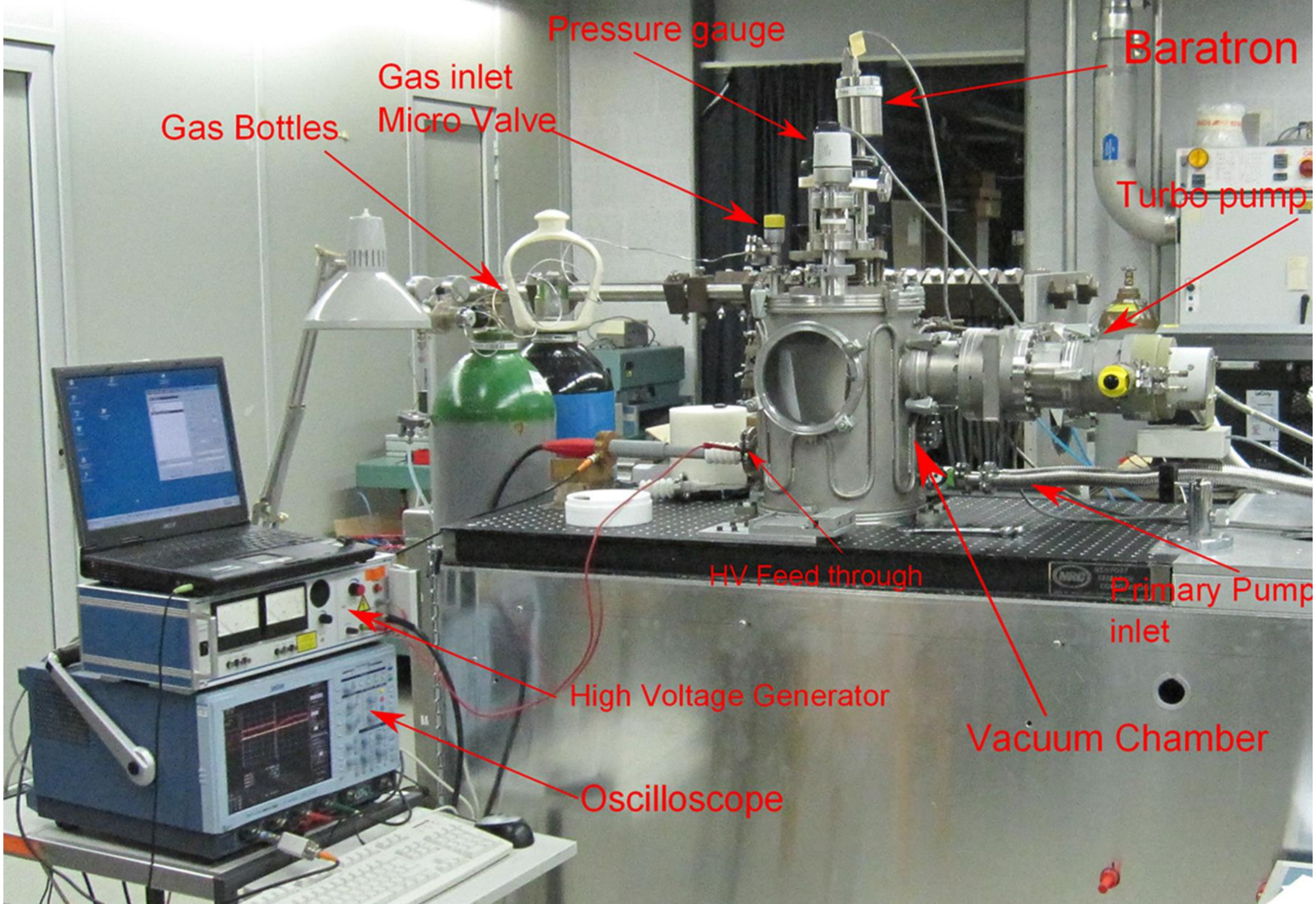
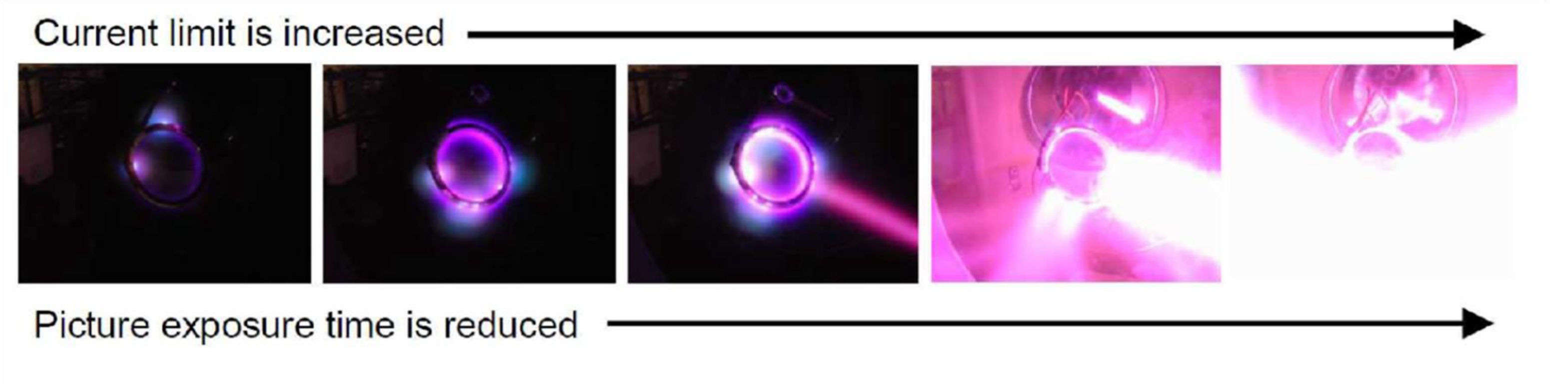

Pressure gauge
Baratron
Gas inlet
Micro Valve
Gas Bottles
Turbo pump
HV Feed through
Primary Pump inlet
High Voltage Generator
Vacuum Chamber
Oscilloscope

Breakdown criterion in gases

- Breakdown can cause an **arc** → current only limited by the impedance of the external circuit!



  - If the supply voltage is maintained (e.g. a solar panel), catastrophic arcing can occur with strong heating and melting of metal components

➢ Must be avoided (especially when in orbit)!

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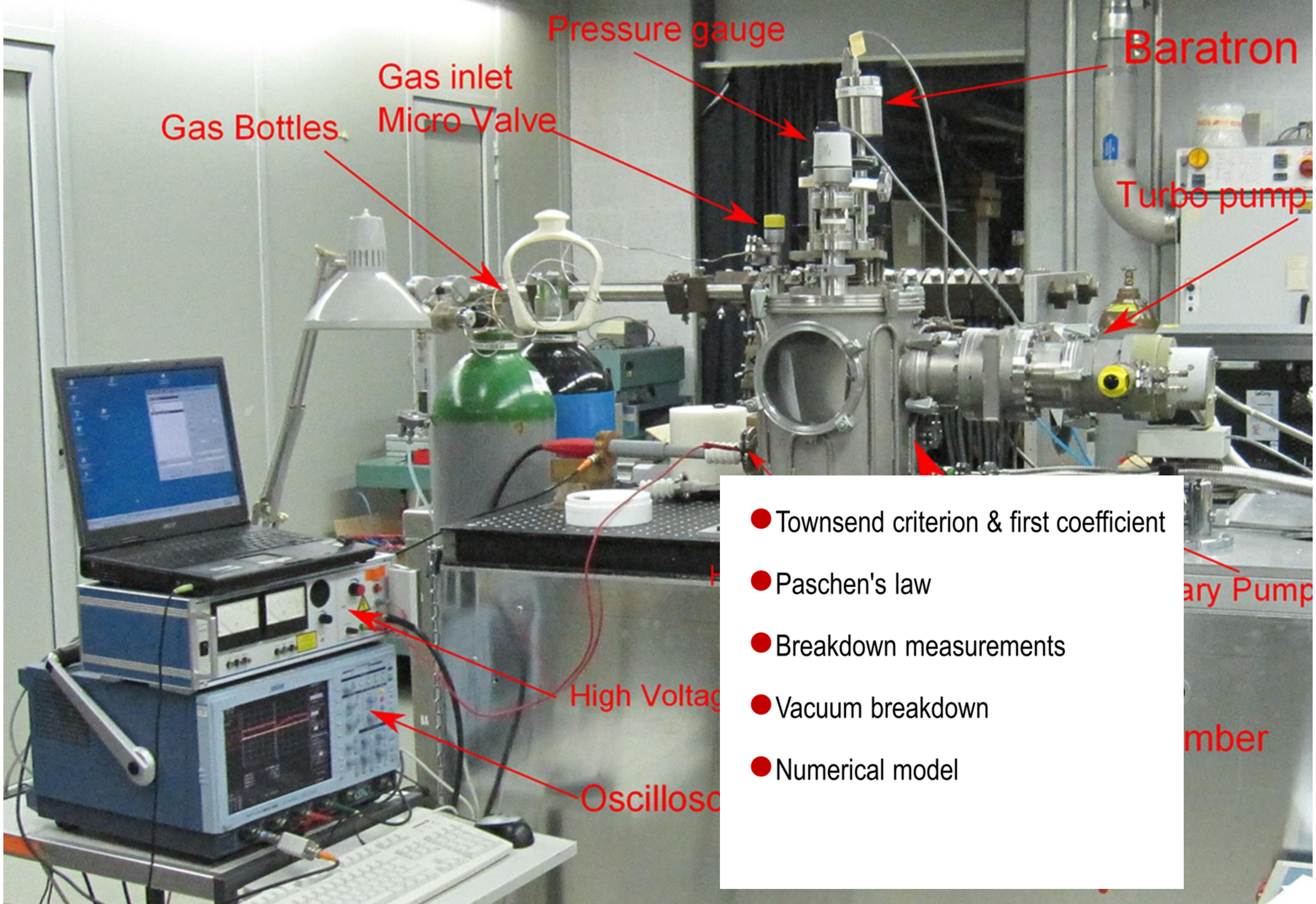


- Townsend criterion & first coefficient
- Paschen's law
- Breakdown measurements
- Vacuum breakdown
- Numerical model

Townsend's first coefficient α

$\lambda_{MFP} = \frac{1}{n\sigma}$ (n: gas density; σ: collision crossection)

How does α depend on the discharge parameters?

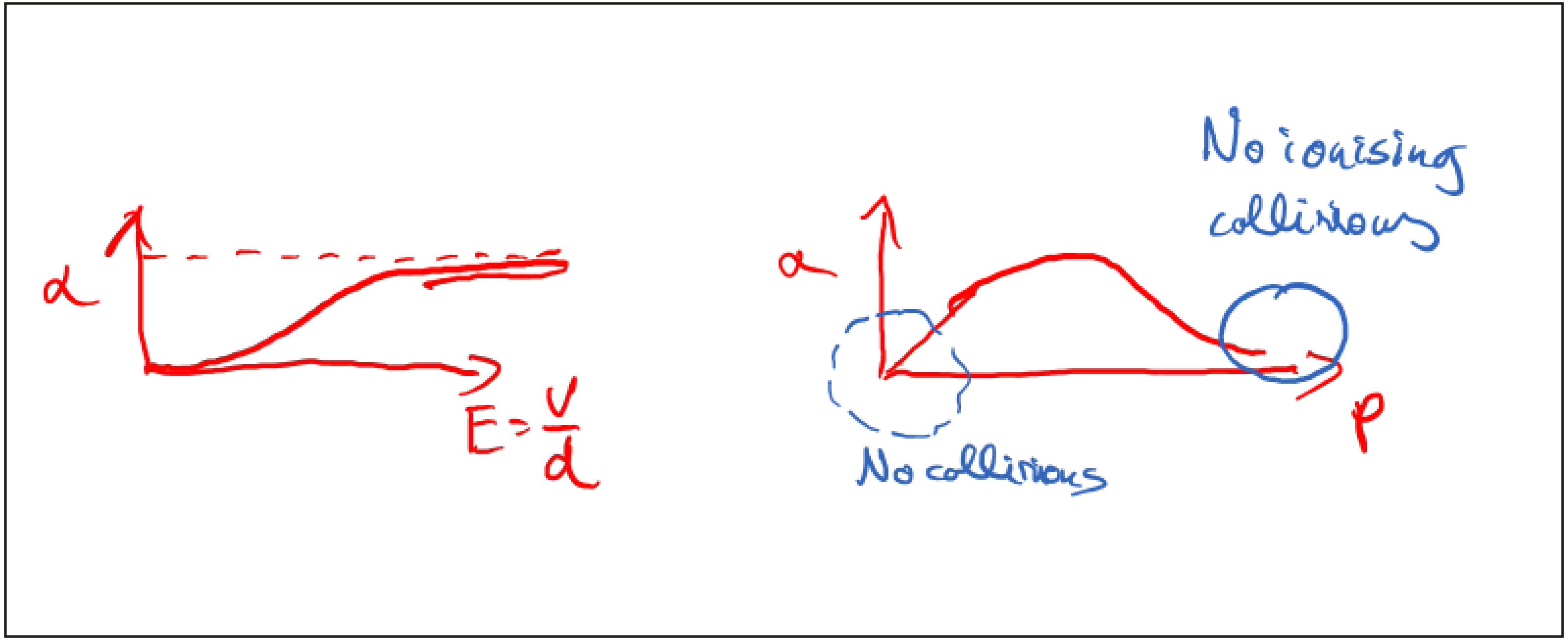
- Number of ionising collisions per electron along distanced dx: $N_{ic} = \alpha dx$
- Number of any collision per electron along distance dx: $N_c = dx/\lambda_{\mathrm{MFP,e}}$
- Probability that collision causes an ionisation: $P_{ic} = e^{-\frac{\varepsilon_i}{eE\lambda_{\mathrm{MFP,e}}}}$

$$N_{ic} = \alpha dx = \underbrace{\frac{dx}{\lambda_{\mathrm{MFP,e}}}}_{N_c} \underbrace{e^{-\frac{\varepsilon_i}{eE\lambda_{\mathrm{MFP.e}}}}}_{P_{ic}}$$

- With $\lambda_{\mathrm{MFP,e}} \propto p^{-1}$, identify: $\alpha = Ap\, e^{-\frac{Bp}{E}}$
- For parallel plates with distance d: $\boxed{\alpha = Ap\, e^{-\frac{Bpd}{V}}}$

Townsend's first coefficient α

- For parallel plates with distance d, $\alpha = Ap\, e^{-\frac{Bpd}{V}}$



Paschen's law: DC breakdown between parallel plates

- Breakdown criterion: $\gamma e^{\alpha d} = \gamma + 1 \quad \Leftrightarrow \quad \alpha d = \ln\left(1 + \frac{1}{\lambda}\right)$
- Substitute expression for α: $Apd \exp\left(-\frac{Bpd}{V_B}\right) = \ln\left(1 + \frac{1}{\lambda}\right)$
- Solve breakdown voltage: $$V_B = \frac{B \cdot pd}{\ln(A \cdot pd) - \ln[\ln(1 + 1/\gamma)]}$$

or equivalently $V_B = \frac{B \cdot pd}{\ln(C \cdot pd)}$; where $C = \frac{A}{\ln(1+1/\gamma)} = cst.$

Paschen's law: The DC breakdown voltage between parallel plates depends only on the product pd for a given gas

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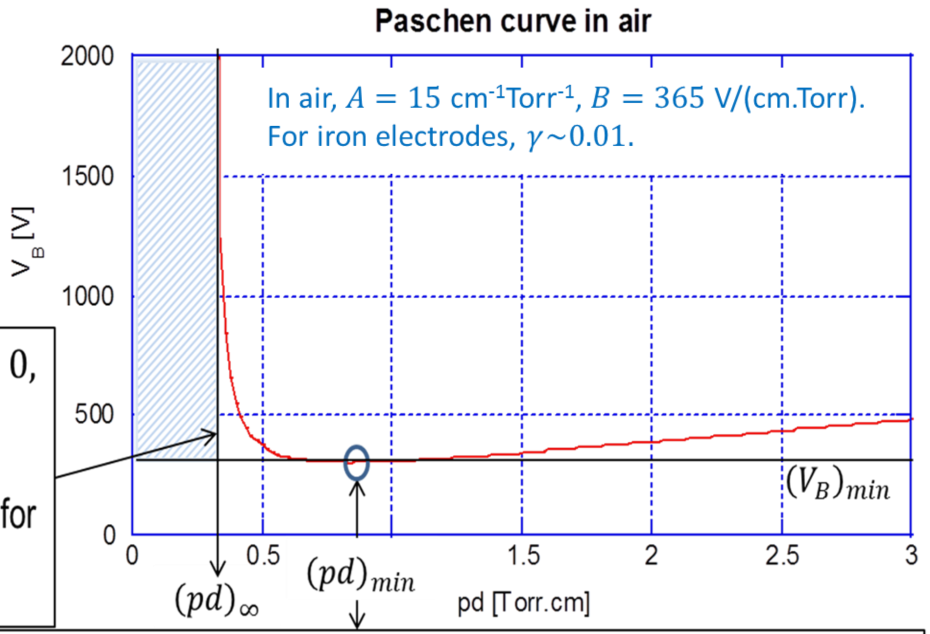
Paschen's law: DC breakdown between parallel plates

- Breakdown voltage

$$V_B = -\frac{B \cdot pd}{\ln(C \cdot pd)}$$

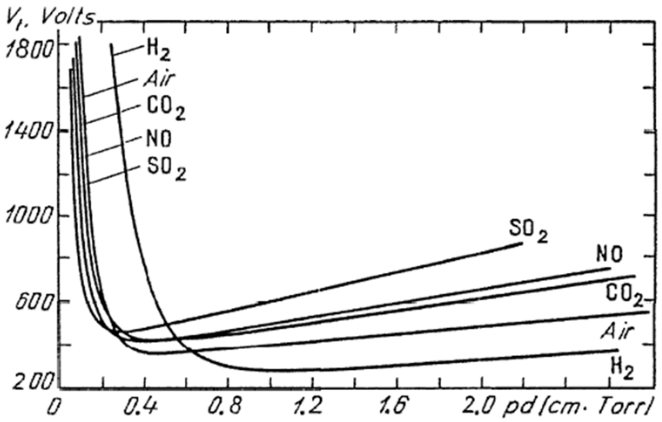
with $C = -\frac{A}{\ln(1+1/\gamma)} = \text{const.}$



1) As $C \cdot pd \to 1, \ln C \cdot pd \to 0$, and $V_B \to \infty$.
"No" breakdown is possible,
i.e. "infinite" breakdown voltage for $pd < (pd)_\infty = \frac{1}{A}\ln\left(1 + \frac{1}{\gamma}\right)$.

2) V_B is minimum for $\ln(C \cdot pd) = 1$,
where $(V_B)_{min} = B \cdot (pd)_{min}$ and $(pd)_{min} = e^1 \cdot (pd)_\infty$

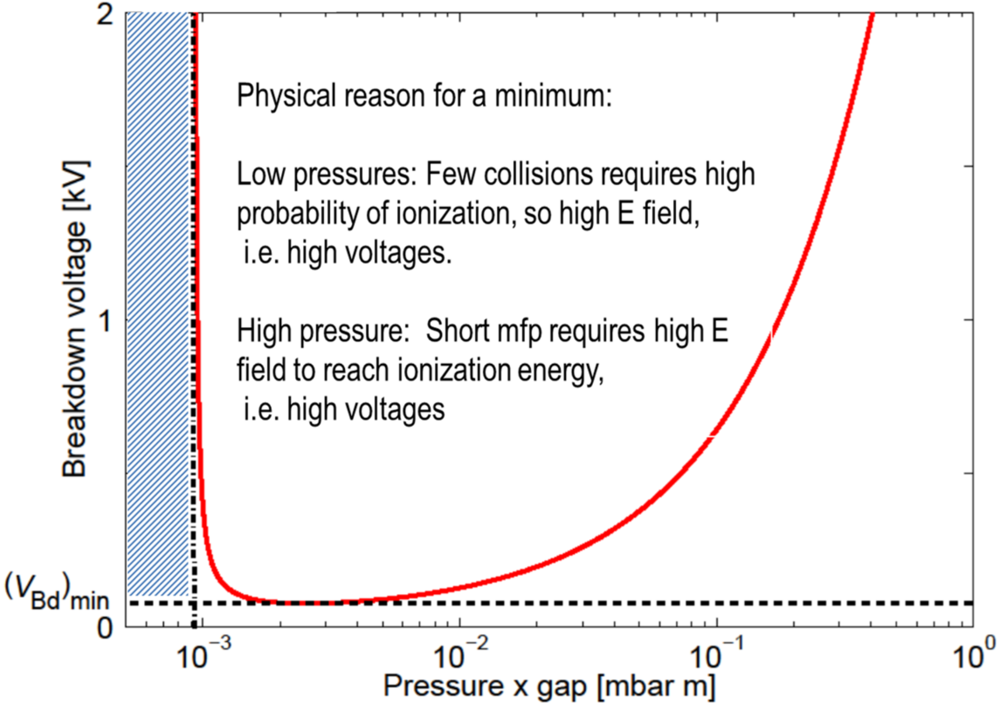
Paschen's law: DC breakdown between parallel plates



- Paschen curve depends on $p \cdot d$
  1. Number of collisions for an electron between electrodes:
     $$d/\lambda \propto p \cdot d$$
  2. Electron collision energy:
     $$eE\lambda = eV\lambda/d \propto 1/(p \cdot d)$$

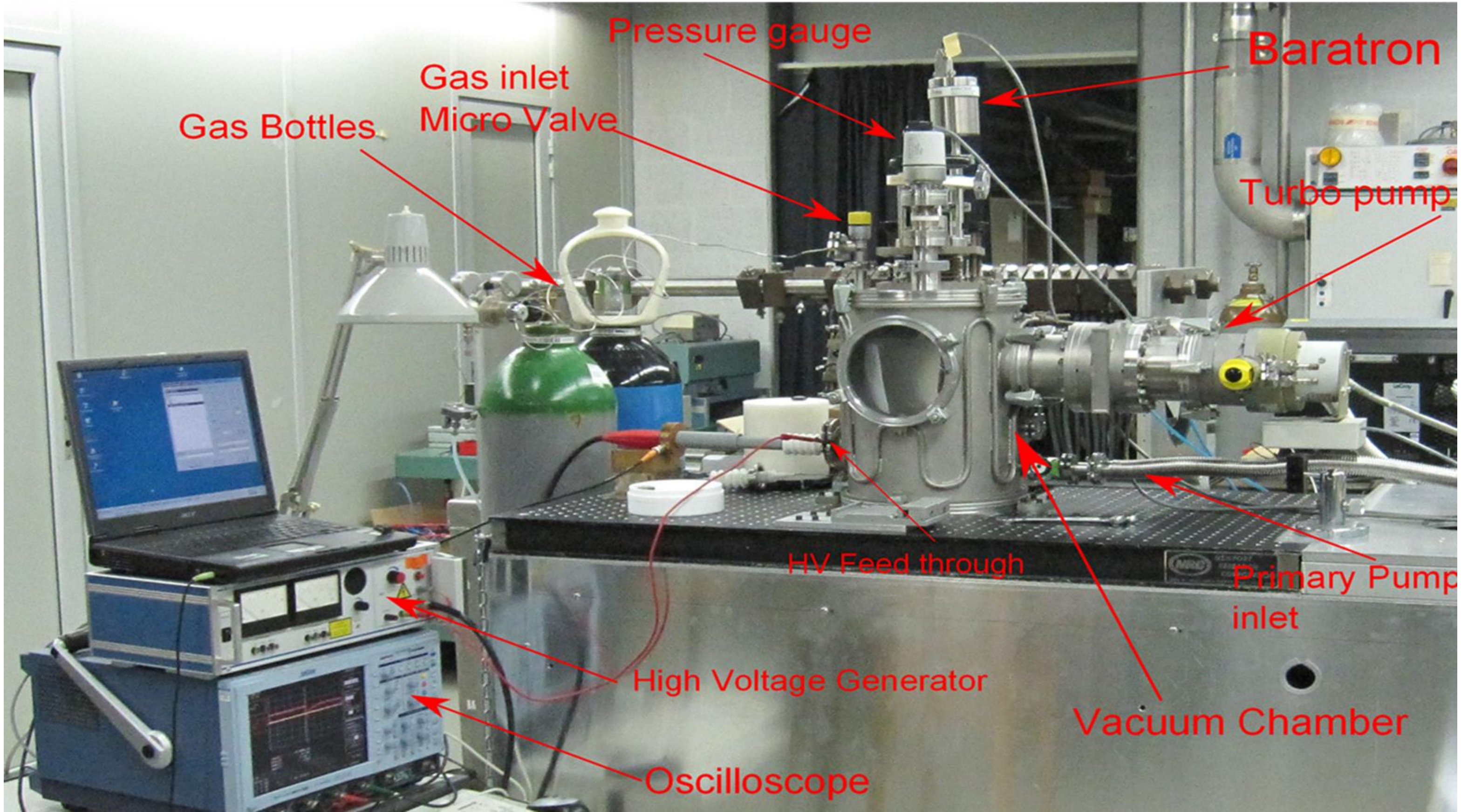
- The form of the curves depends on
  - α, which depends on the gas type
  - γ, which depends on the gas type and the electrode material

Paschen's law: DC breakdown between parallel plates



Breakdown measurements for real applications

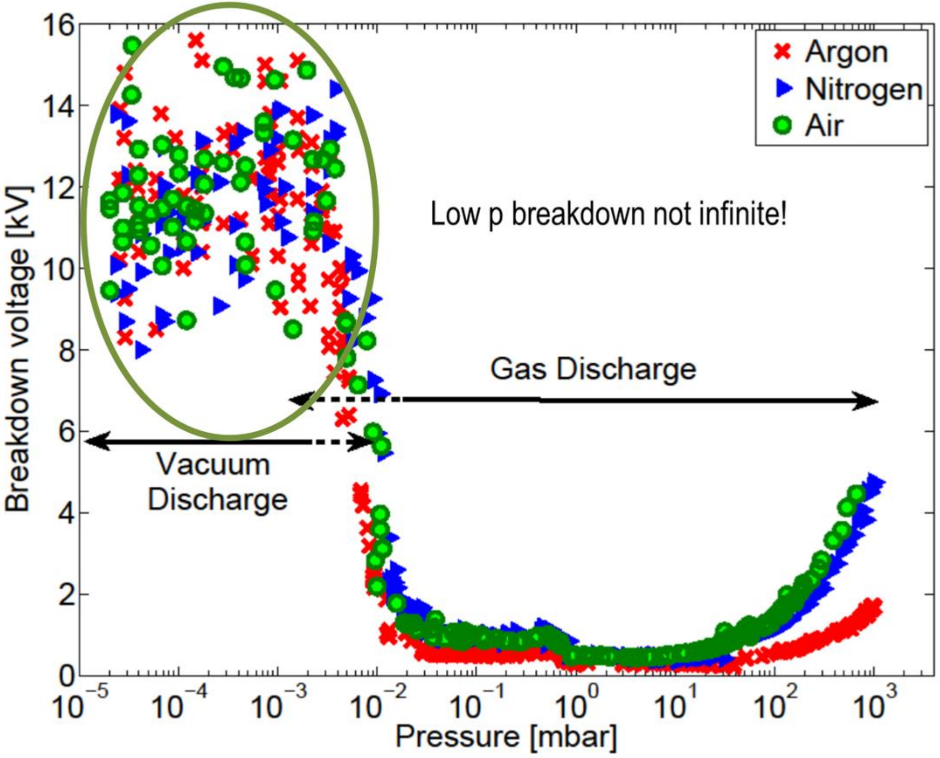
R. Schnyder, et al., *J. Phys. D: Appl. Phys*. **46** (2013) 285205



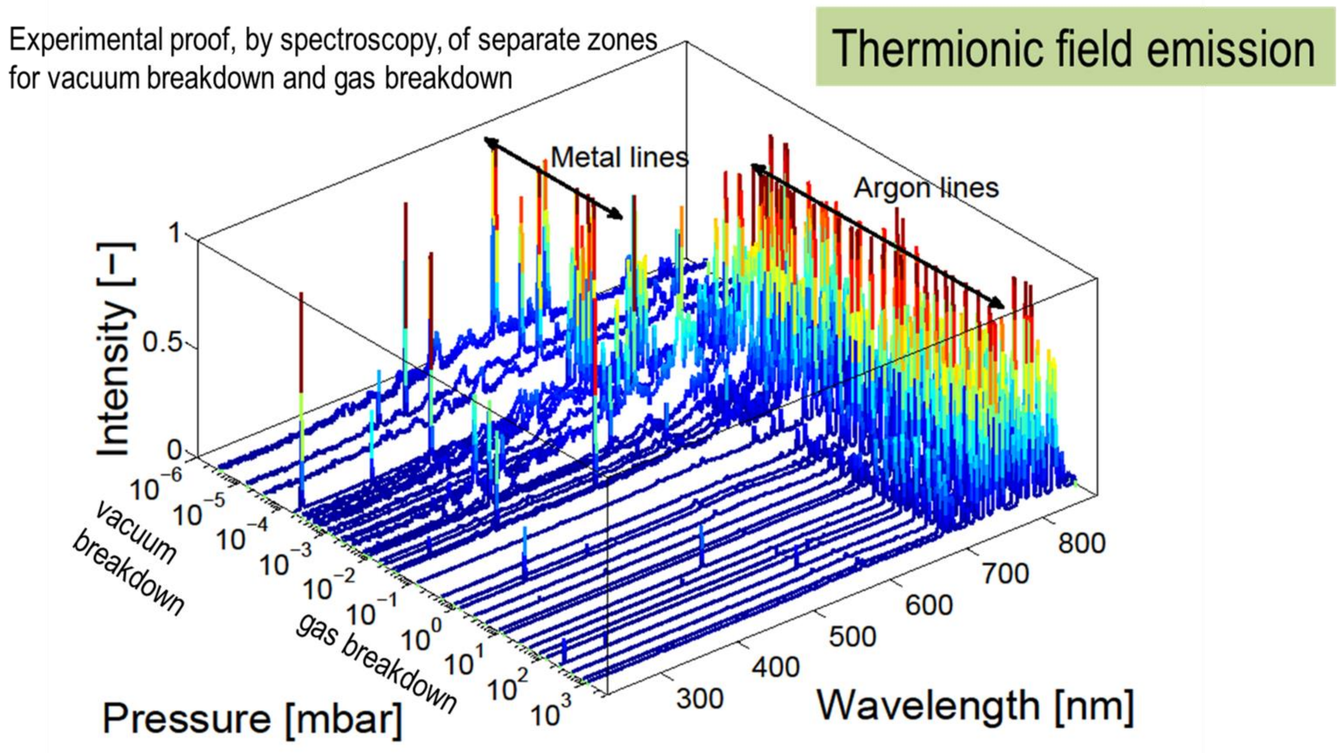
Breakdown measurements

H. Reimerdes

Laboratory test of slip-ring assembly

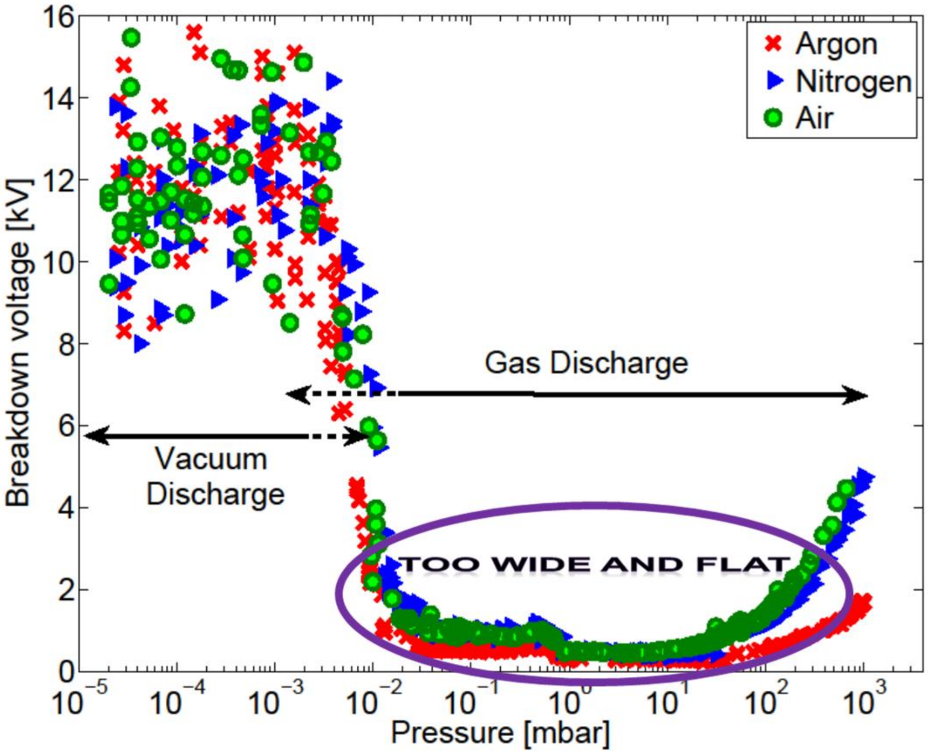


Vacuum breakdown

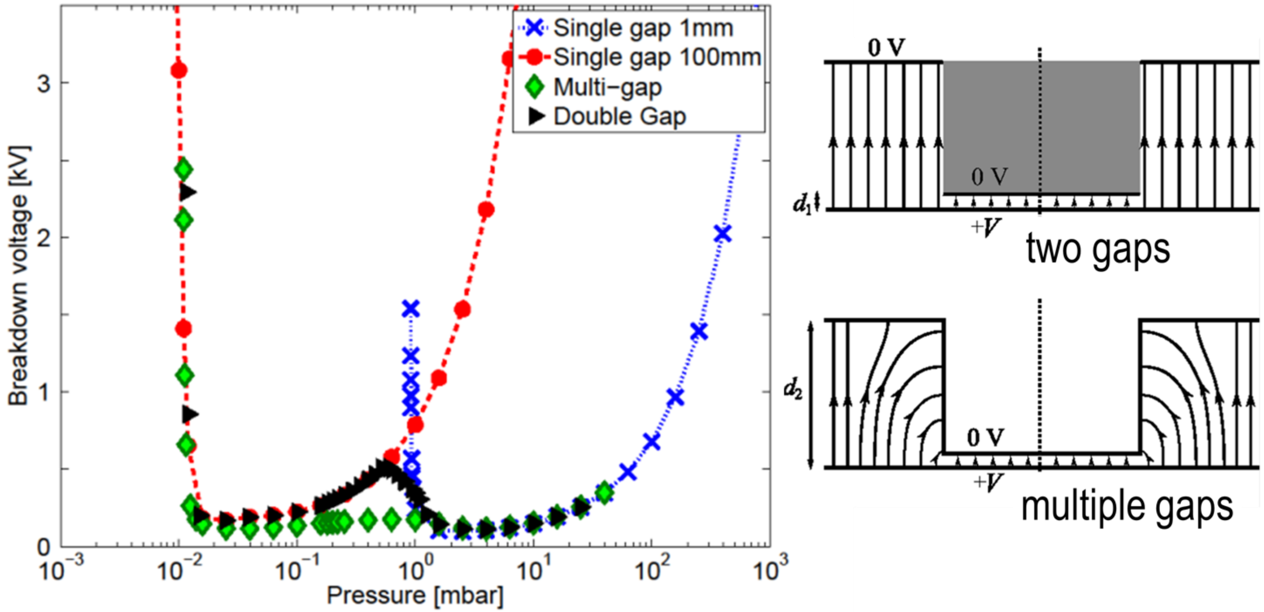


Breakdown measurements

Laboratory test of slip-ring assembly



Breakdown numerical simulations



➢ Multiple-gaps yield low breakdown voltage over a wide range of pressures

Summary of breakdown in low pressure gases

- Background ionisation current: $i_0 = \dot{N}_0 e$
- Avalanche ionisation: $i = i_0 e^{\alpha d}$
- Secondary emission: $i = \frac{i_0 e^{\alpha d}}{1-\gamma\left(e^{\alpha d}-1\right)}$
- Breakdown criterion: $\gamma e^{\alpha d} = \gamma + 1$
- Townsend's first coefficient: $\alpha = Ape^{-\frac{Bp}{E}}$
- Paschen's law for parallel plates: $V_B = \frac{B \cdot pd}{\ln(C \cdot pd)}$
- Vacuum and multi-gap breakdown