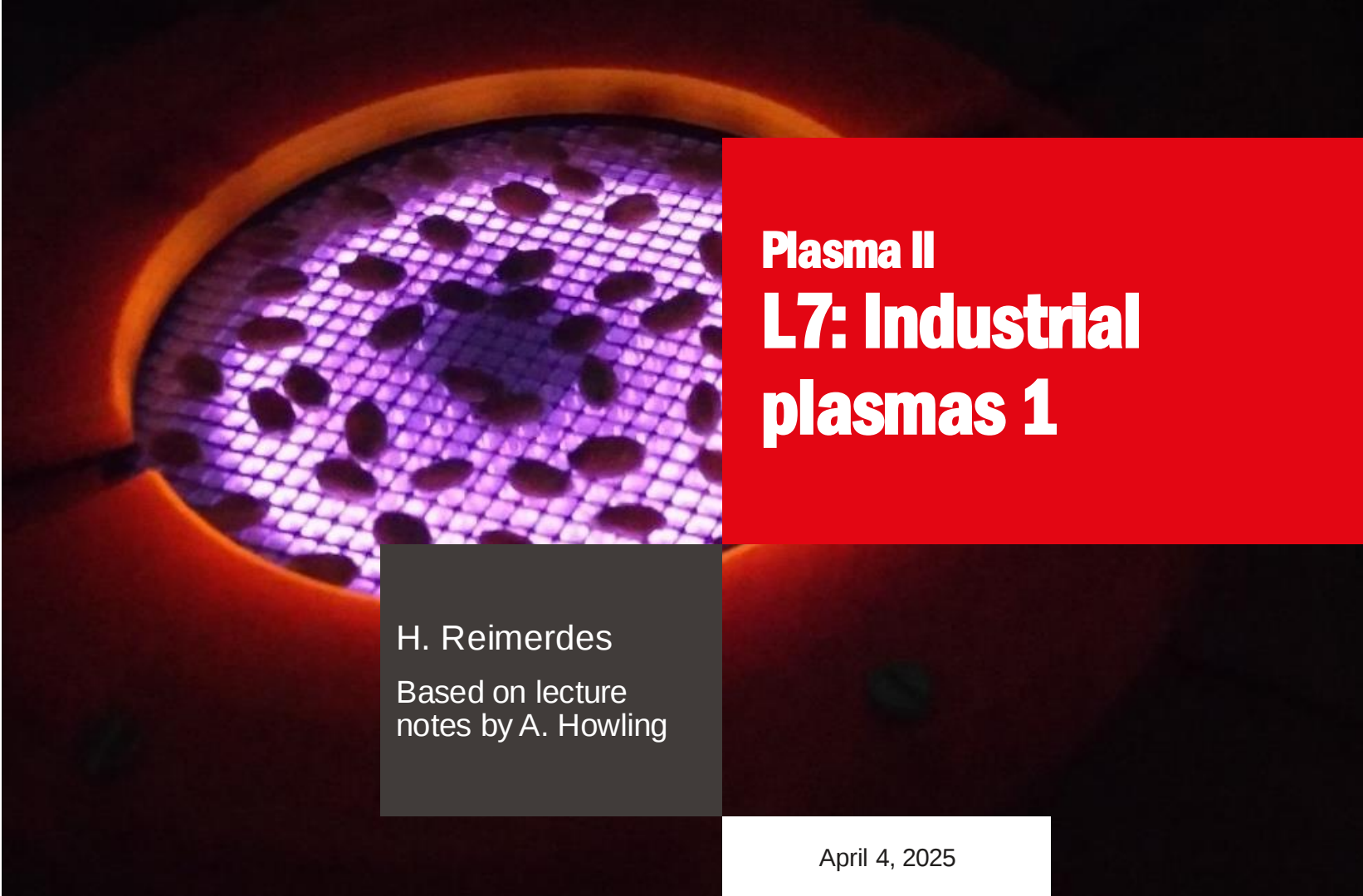




Plasma II

L7: Industrial plasmas 1

H. Reimerdes

Based on lecture
notes by A. Howling

1. Introduction to basic industrial plasmas

- Plasma medicine

2. Breakdown and Paschen's law

- Communication satellite

3. Sheath and plasma etching

- Microelectronics

4. Plasma with insulating electrodes

- Large area displays/solar cells

L7

L8

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

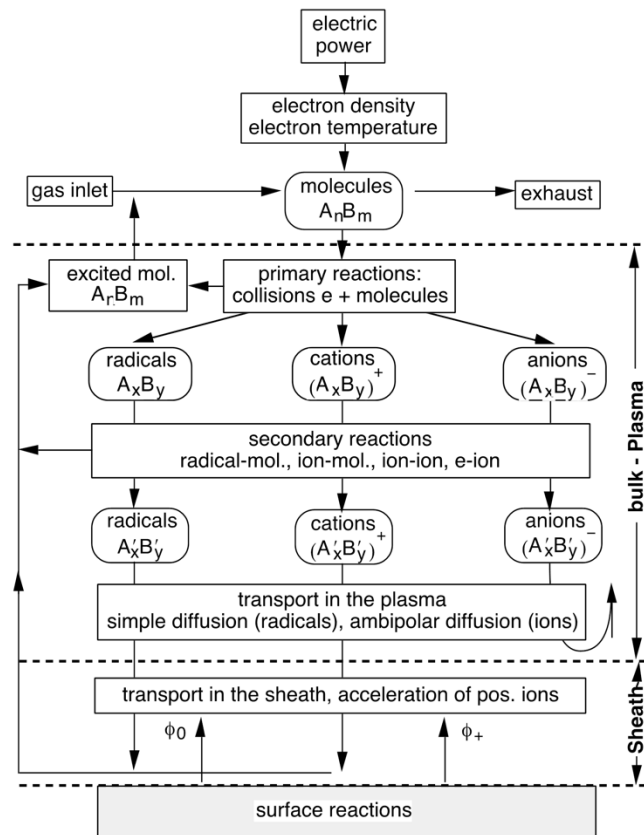
Industrial plasma applications

- 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

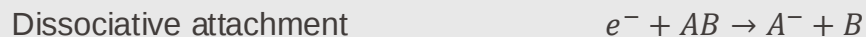
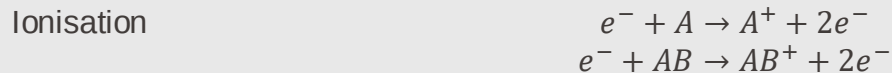
- High pressure (order of mbar) of neutrals
- Low degree of ionisation $\sim 10^{-6}$ to 10^{-3}
- Collisional damping, no waves
- Often no magnetic field, no MHD



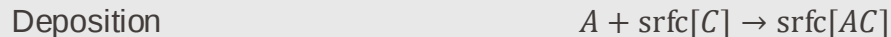
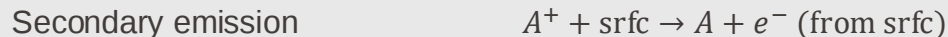
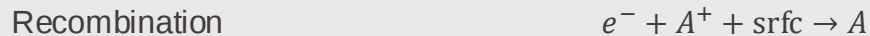
L8

Different types of reactions

Gas phase reactions (homogeneous) involving electrons



Surface reactions (heterogeneous)



■ Transport of species to surface

- Neutrals: Diffusion of species A with $-D_A \nabla n_A$
- Ions: Ion flux across sheath (see L8) with $n^+ v_{\text{Bohm}}$

Example: Simple oxygen plasma

- Some binary reactions:

Number	Reaction	Rate Constant (cm ³ /s)
<i>Reactions among e, O₂, O₂⁺, and O⁺</i>		
1	e + O ₂ momentum transfer	4.7E-8T _e ^{0.5}
2	e + O ₂ → O ⁻ + O	8.8E-11 exp(-4.4/T _e)
3	e + O ₂ → 2O + e	4.2E-9 exp(-5.6/T _e)
4	e + O ₂ → O ₂ ⁺ + 2e	9.0E-10T _e ^{0.5} exp(-12.6/T _e)
5	e + O ⁻ → O + 2e	2.0E-7 exp(-5.5/T _e)
6	e + O ₂ ⁺ → 2O	5.2E-9/T _e
7	O ⁻ + O ₂ ⁺ → O + O ₂	(0.96, 2)E-7(300/T) ^{0.5}
8	O ⁻ + O → O ₂ + e	(1.4, 5)E-10
9	O ⁻ + O ₂ ⁺ → 3O	1E-7
<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	5.3E-10T _e ^{0.9} exp(-20/T _e)
12	e + O → O ⁺ + 2e	9.0E-9T _e ^{0.7} exp(-13.6/T _e)
13	O ⁻ + O ⁺ → 2O	(2.7, 2)E-7(300/T) ^{0.5}
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	1.7E-9 exp(-3.1/T _e)
16	e + O ₂ [*] → e + O ₂	5.6E-9 exp(-2.2/T _e)
17	O ₂ [*] + O ₂ → 2O ₂	2.2E-18(T/300) ^{0.8}
18	O ₂ [*] + O → O ₂ + O	(1.0, 7)E-16
<i>Addition of metastable O(¹D)</i>		
19	e + O ₂ → O + O ⁺ + e	5.0E-8 exp(-8.4/T _e)
20	e + O → O ⁺ + e	4.2E-9 exp(-2.25/T _e)
21	e + O ⁺ → e + O	8E-9
22	e + O ⁻ → O ⁺ + 2e	9.0E-9T _e ^{0.7} exp(-11.6/T _e)
23	O ⁺ + O → 2O	8.0E-12
24	O ⁺ + O ₂ → O + O ₂	(6.4, 7.0)E-12 exp(67/T)
25	O ⁺ + O ₂ → O + O ₂ ⁺	1.0E-12
<i>Addition of selected reactions for O₂⁻ and O₃</i>		
26	O ⁻ + O ₂ → O ₃ + e	5E-15
27	e + O ₃ → O ₂ ⁻ + O	1E-9
28	O ⁻ + O ₂ ⁺ → O ₃ + e	3E-10
29	O ⁻ + O ₂ ⁺ → O ₂ ⁻ + O	1E-10
30	O ₂ ⁻ + O ₂ ⁺ → 2O ₂	2E-7(300/T) ^{0.5}
31	O ₂ ⁻ + O ⁺ → O ₂ + O	2E-7(300/T) ^{0.5}
32	O ₃ + O ₂ → O ₂ + O + O ₂	7.3E-10 exp(-11400/T)
33	O ₃ + O → 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: $m \ll M \rightarrow \delta_{\max} \sim \frac{4m}{M} \ll 1$
- For an ion hitting an atom: $m \approx M \rightarrow \delta_{\max} \sim 1$

- 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: Electric force $\times$ electron drift speed

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

Drift velocity

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: Electric force $\times$ electron drift speed

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

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

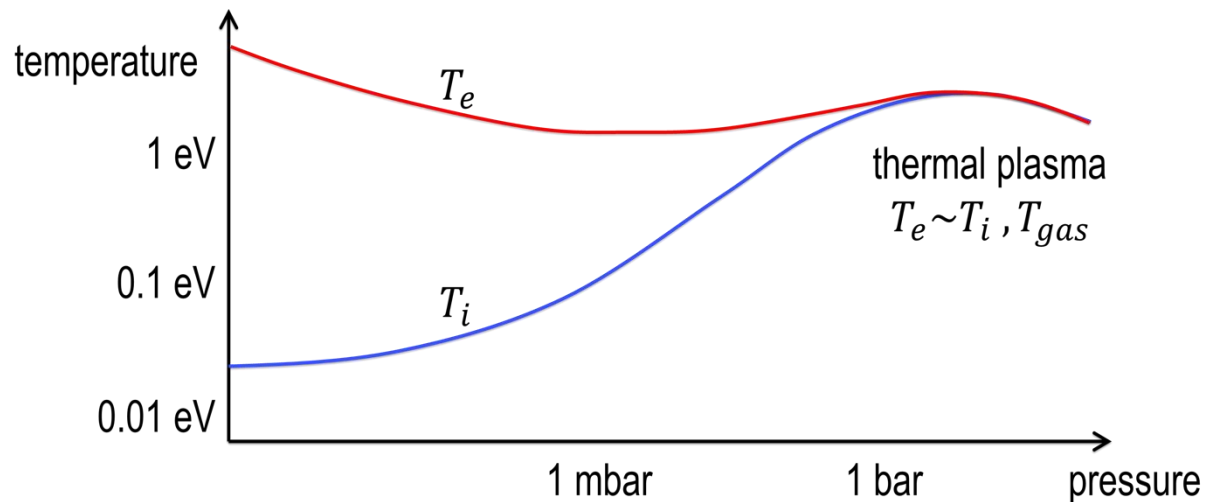
$$\bar{P}_{e,\text{loss}} = \frac{3}{2} \delta e (T_e - T_{\text{gas}}) \nu^{e/n}$$

- Steady-state

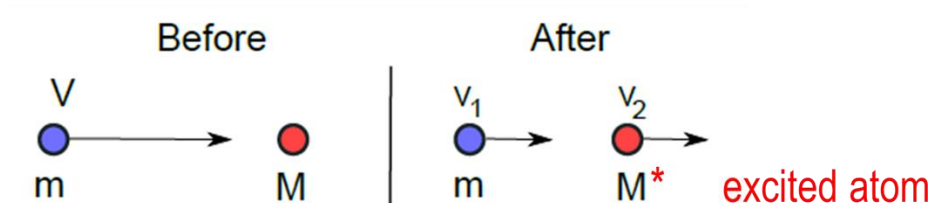
$$(T_e - T_{\text{gas}}) = \frac{2eE^2}{3\delta m_e (\nu^{e/n})^2} \propto \left(\frac{1}{\text{pressure}} \right)^2$$

Low pressure, non-equilibrium plasma

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



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 ($T_e \sim 2\text{eV} \approx 23,000\text{K}$), non-equilibrium plasma ($T_e \gg T_{\text{gas}}$)
- High temperature plasma chemistry on low temperature substrates (e.g. glass, plastic, people)
 - Rate of chemical reactions

$$k = Ae^{-\frac{E_a}{k_B T}} \quad \text{Arrhenius' equation}$$

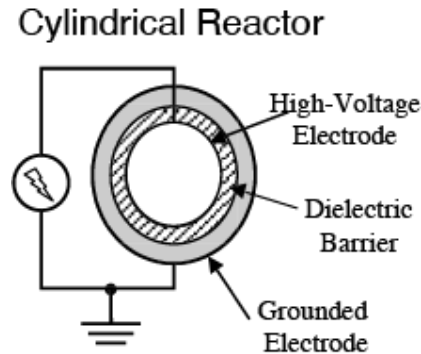
- + With activation energy E_A and reaction specific pre-exponential factor A

→ See exercise 2 for numerical values

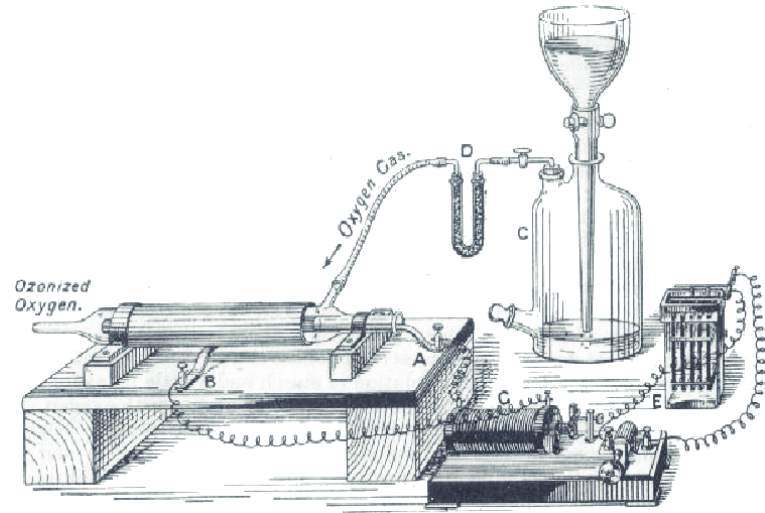
- Low temperature plasmas can generate **reactive species**
 - Reactive oxygen species (**ROS**), e.g. peroxides and superoxides
 - Reactive nitrogen species (**RNS**)
- Low temperature plasma emit in the UV
- Effects on tissue and cells
 - Sterilisation, decontamination, blood coagulation
- Application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



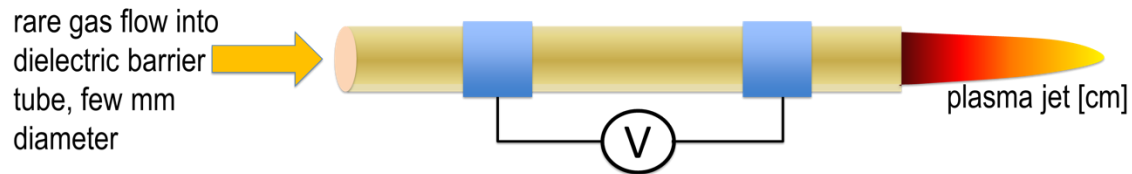
[Wagner, et al., Vacuum 73 (2003)]



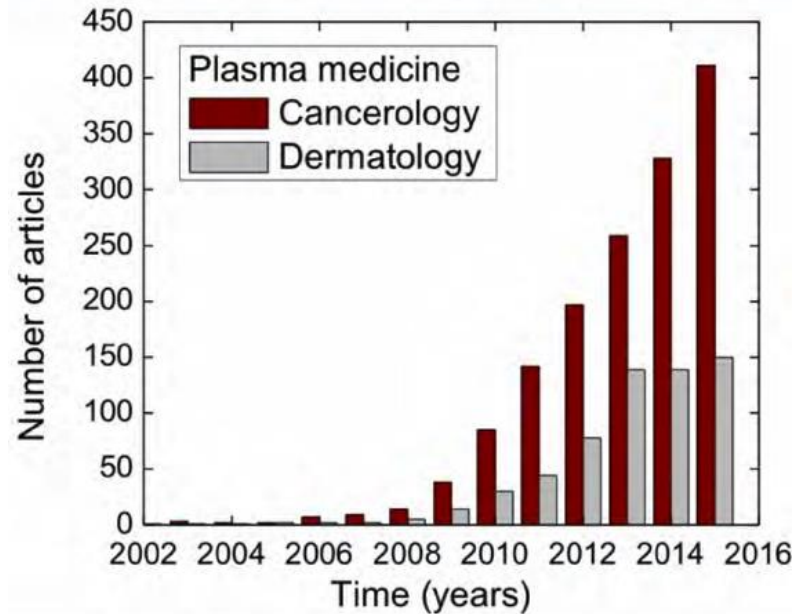
- Suitable for high gas pressure
- Operated between line frequency and 10MHz

Plasma delivery for medical applications

- Example tool: Low temperature DBD plasma jet in air



- Complex, but rapidly evolving new field of research



Excursus: Units of temperature in plasma physics

- 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 $k_B = 1.38 \times 10^{-23} \text{ J/K}$ 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**

1. Introduction to basic industrial plasmas

- Plasma medicine

2. Breakdown and Paschen's law

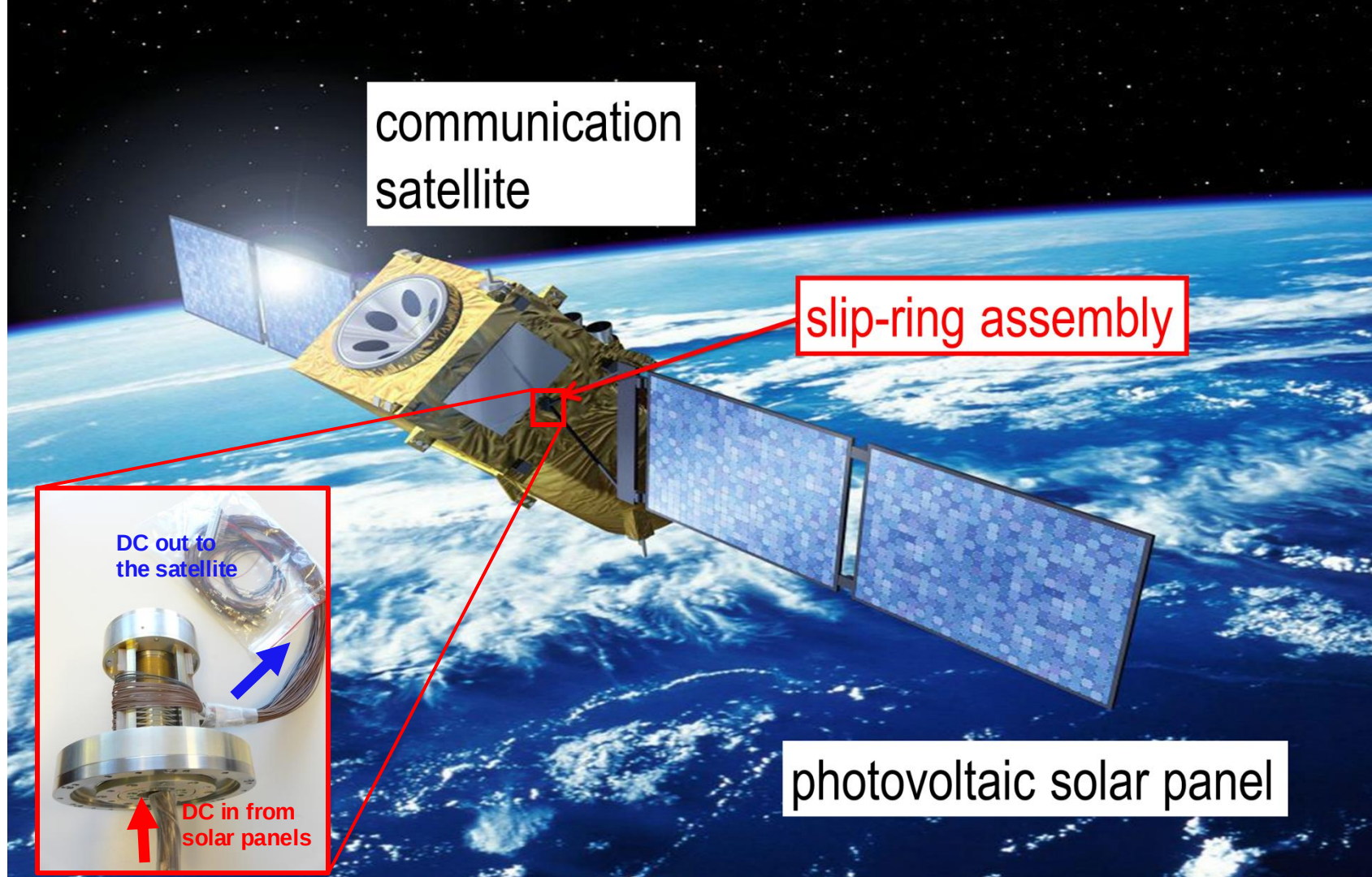
- **Communication satellite**
 - Background ionization
 - First Townsend coefficient
 - Second Townsend coefficient
 - Breakdown criterion in gases

3. Sheath and plasma etching

- Microelectronics

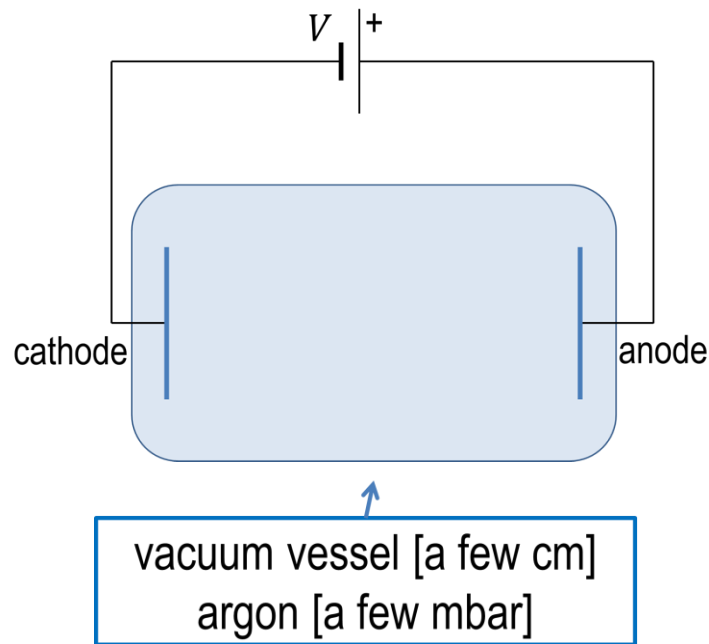
4. Plasma with insulating electrodes

- Large area displays/solar cells



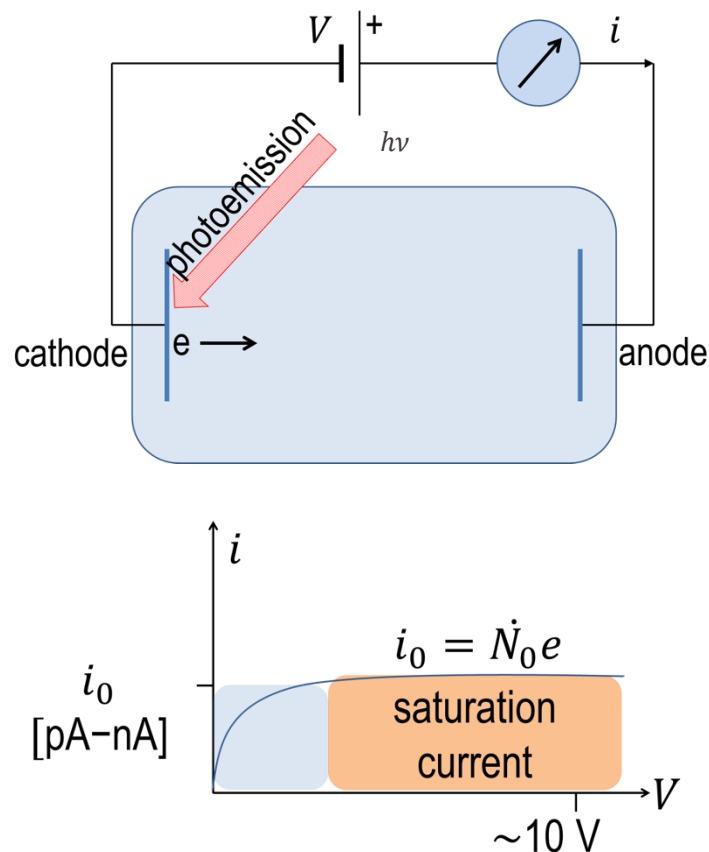
Background ionisation

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



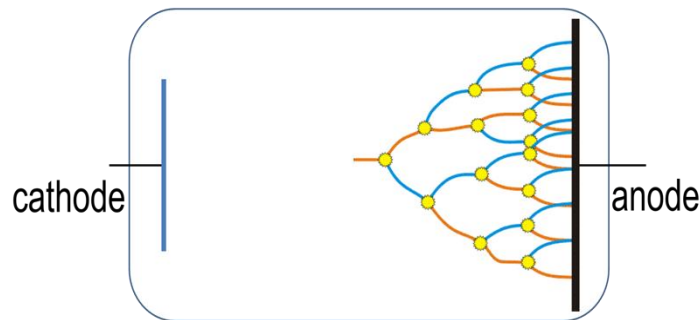
Background ionisation

- 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



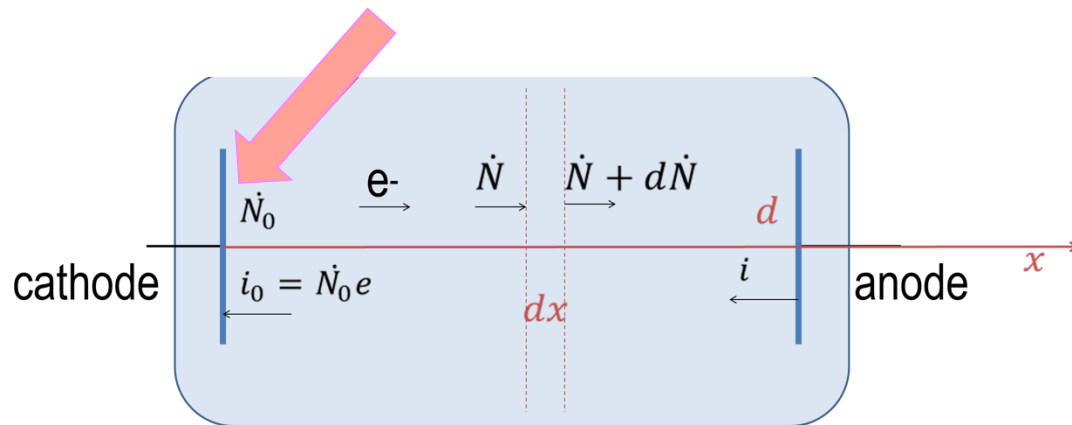
First Townsend coefficient α

- Increase voltage further
 - Ionisation by electron impact creates more electrons
$$e^- + \text{Ar} \rightarrow 2e^- + \text{Ar}^+$$
 - 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

- Evolution of the electron current



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

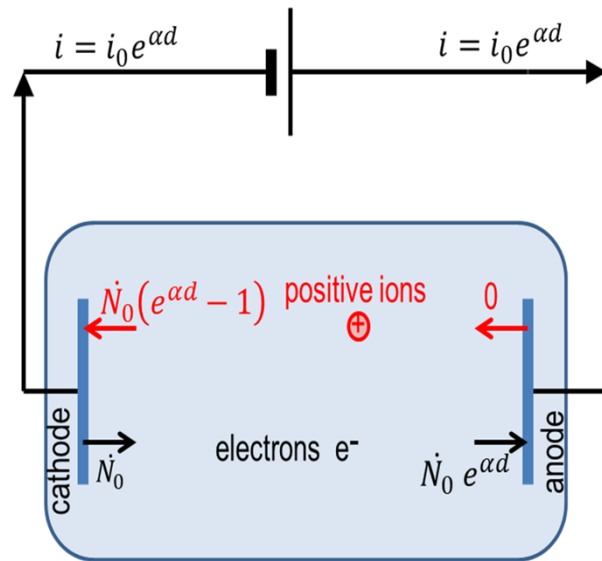
Integrate from cathode to plane at x : $\int_{\dot{N}_0}^{\dot{N}} \frac{d\dot{N}}{\dot{N}} = \int_0^x \alpha dx$

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

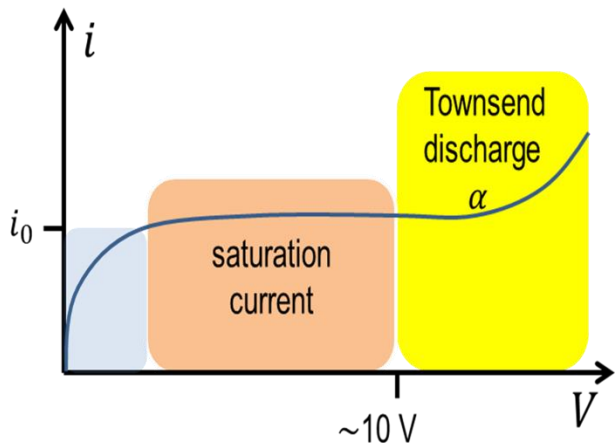
- Continuity of current



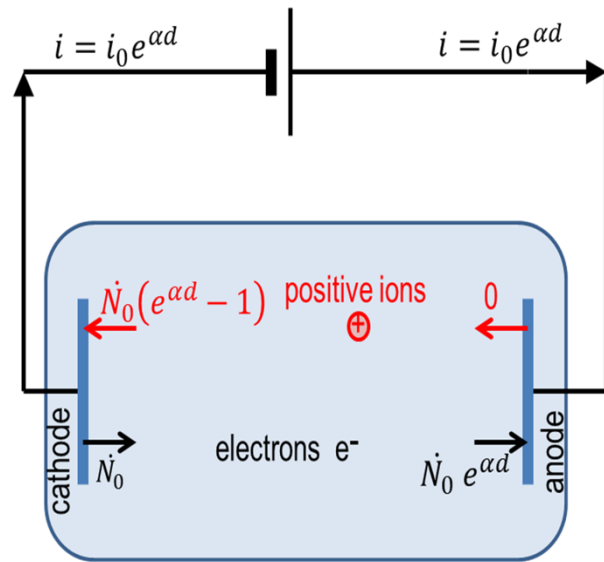
The current crossing any plane is everywhere the same,
 $i = i_0 e^{\alpha d}$

Townsend discharge

- Continuity of current



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



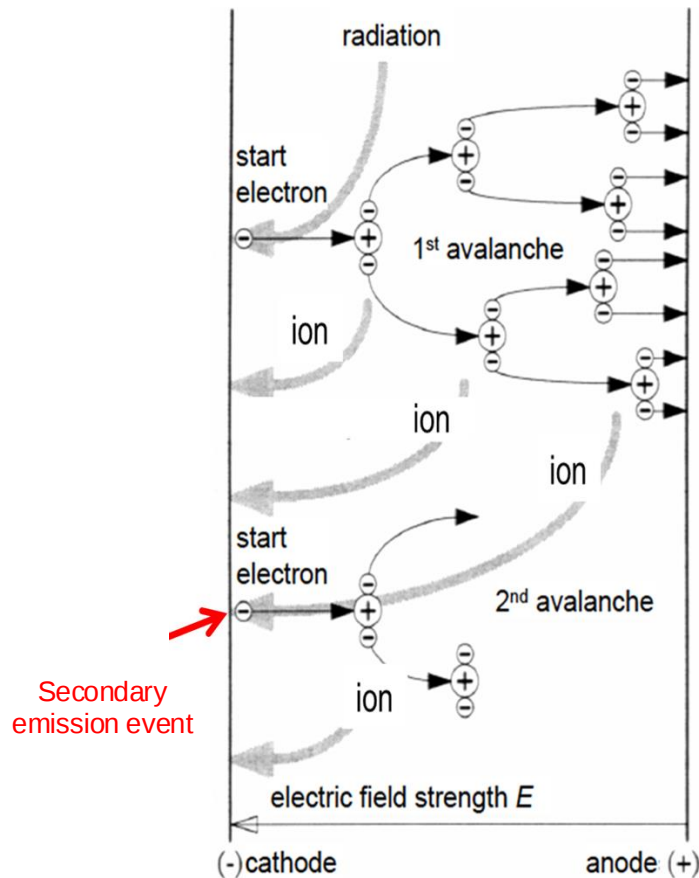
The current crossing any plane is everywhere the same,
 $i = i_0 e^{\alpha d}$

Second Townsend coefficient γ

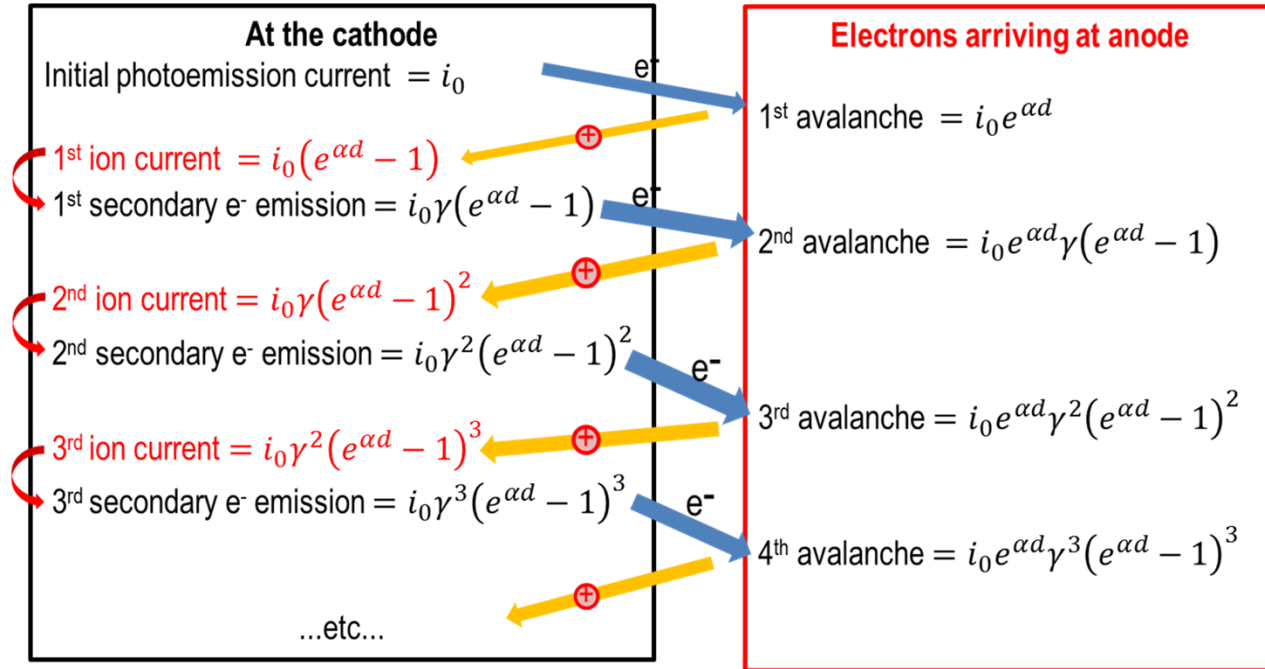
- Current can increase even more strongly due to secondary emission
- Townsend's second ionisation coefficient**

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

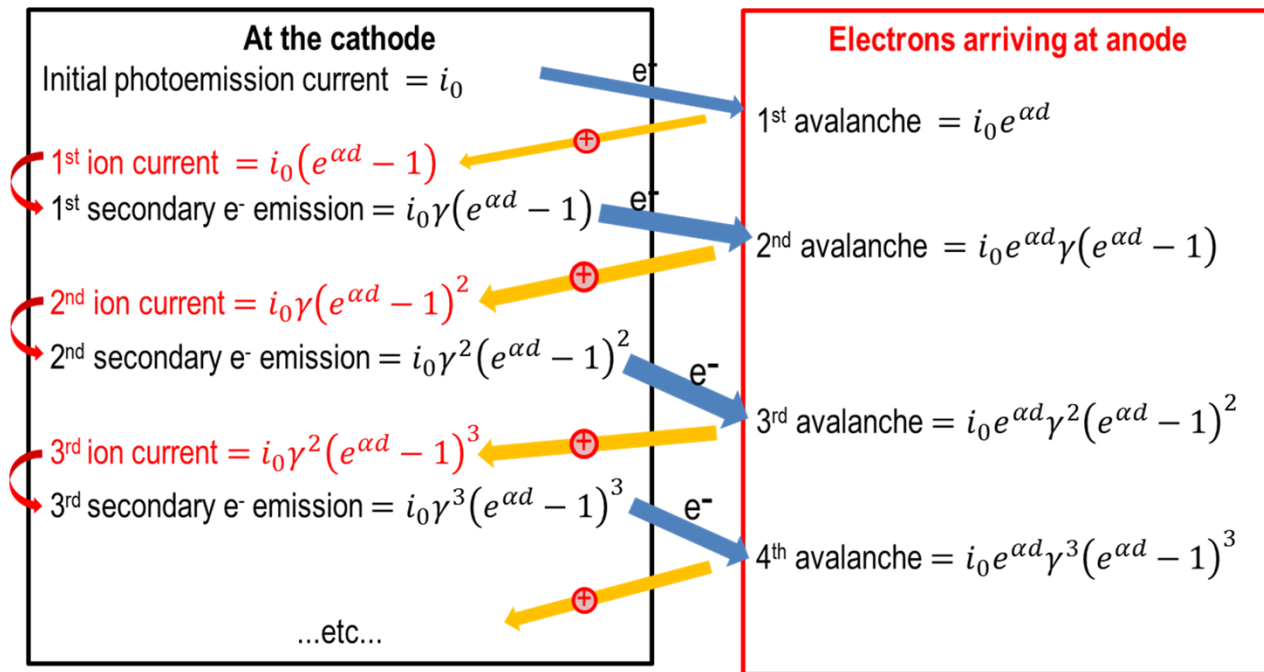
- Depends on gas type and electrode material (e.g. work function)



Second Townsend coefficient γ



Second Townsend coefficient γ



➤ Sum of infinite series at anode:

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

Breakdown criterion in gases

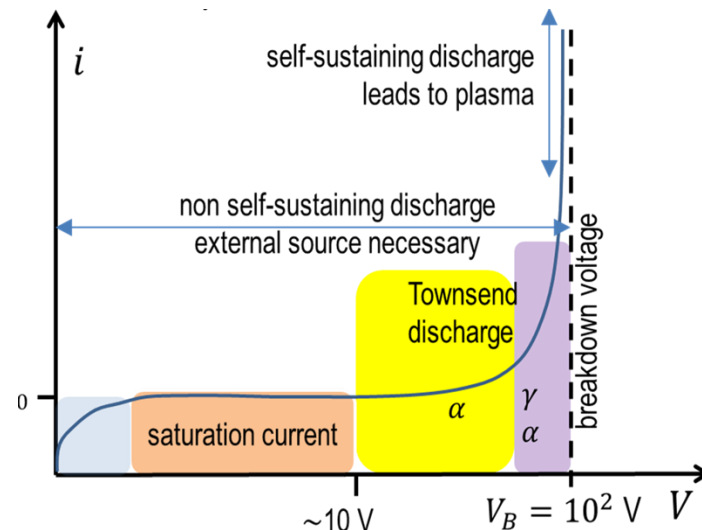
- Current

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

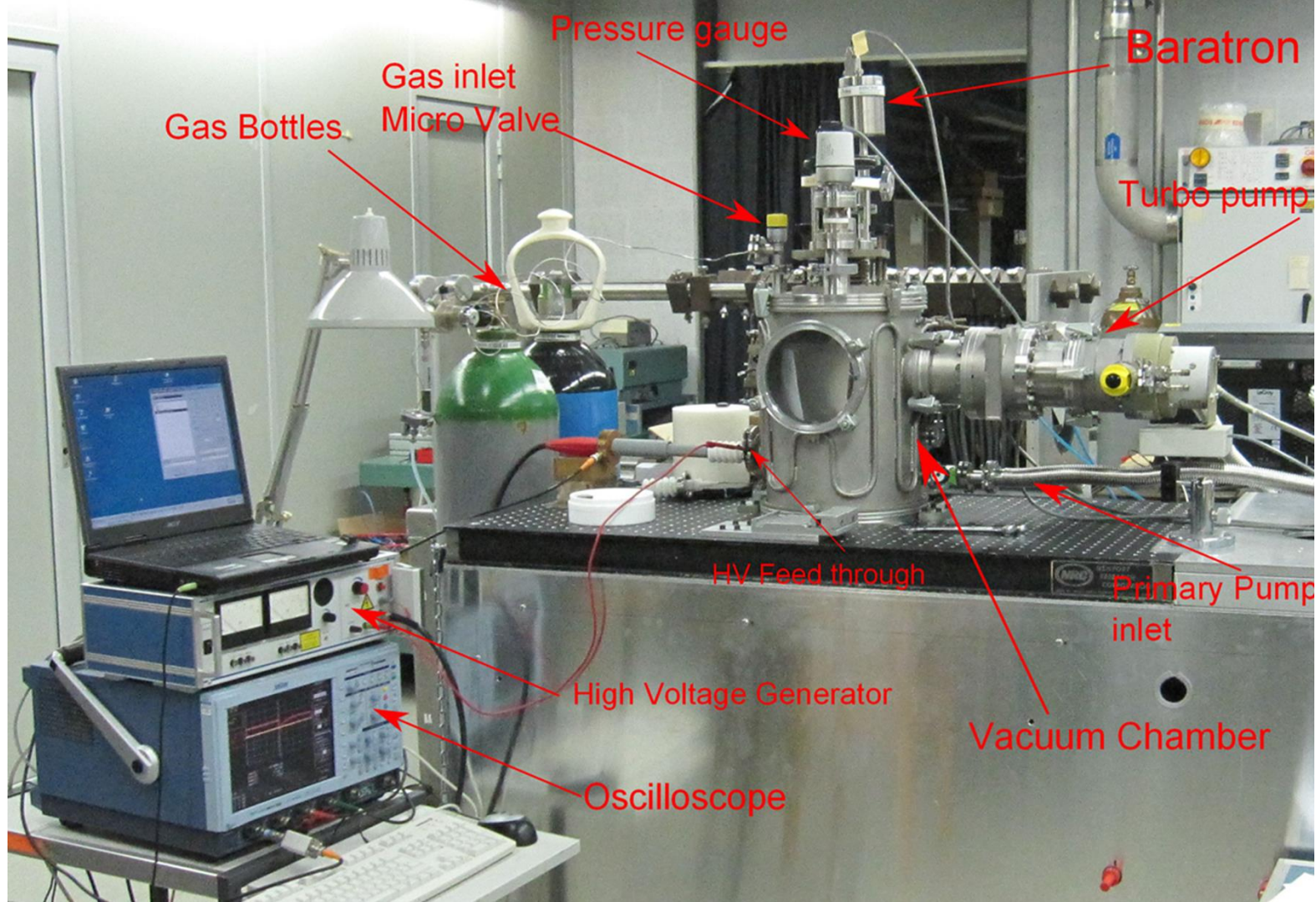
- Townsend criterion for breakdown*

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

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

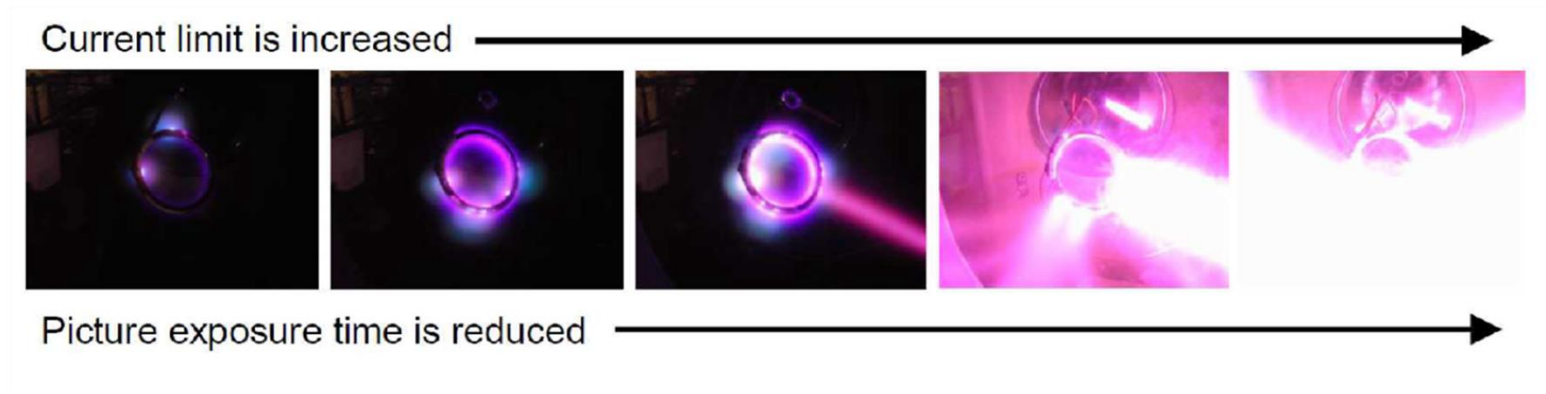


- The gas 'breaks down' and becomes a self-sustained discharge $\rightarrow$ independent of external source i_0
 - $\gamma e^{\alpha d}$: number of secondary electrons emitted per primary electron
 - Replace each primary electron with a new secondary electron



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)!

Townsend's first coefficient α

How does α depend on the discharge parameters?

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

$$N_{ic} = \alpha dx = \frac{dx}{\lambda_{\text{MFP},e}} e^{-\frac{\epsilon_i}{eE\lambda_{\text{MFP},e}}}$$

- With $\lambda_{\text{MFP},e} \propto p^{-1}$, identify: $\alpha = Ap e^{-\frac{Bp}{E}}$

- For parallel plates with distance d :

$$\alpha = Ap e^{-\frac{Bpd}{V}}$$

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

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

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

Paschen's law: DC breakdown between parallel plates

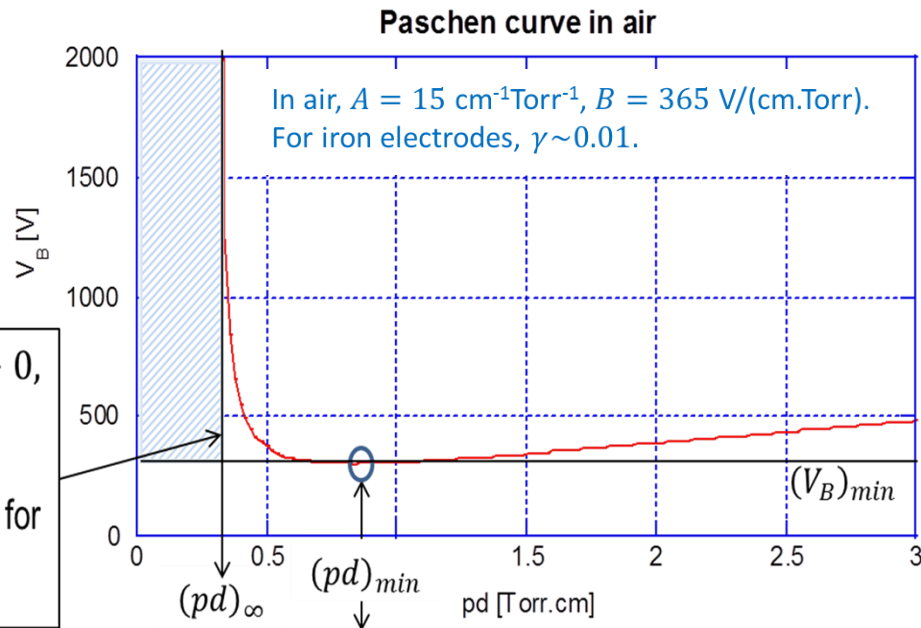
- Breakdown voltage

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

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

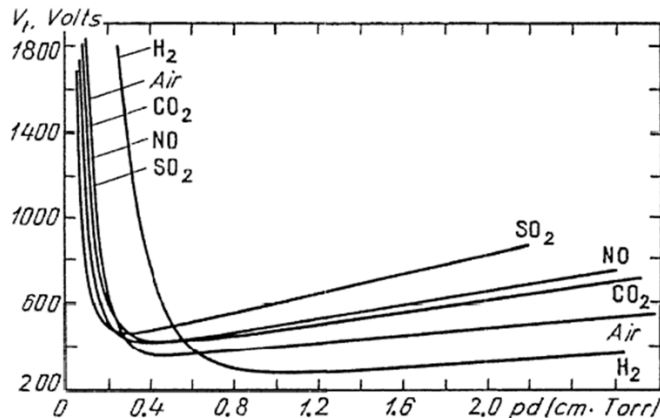
1) As $C \cdot pd \rightarrow 1$, $\ln C \cdot pd \rightarrow 0$, and $V_B \rightarrow \infty$.

"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 $(pd)_{\min} = e \cdot (pd)_\infty$

Paschen's law: DC breakdown between parallel plates



- Paschen curve depends on $p \cdot d$

1. Number of collisions for an electron between electrodes:

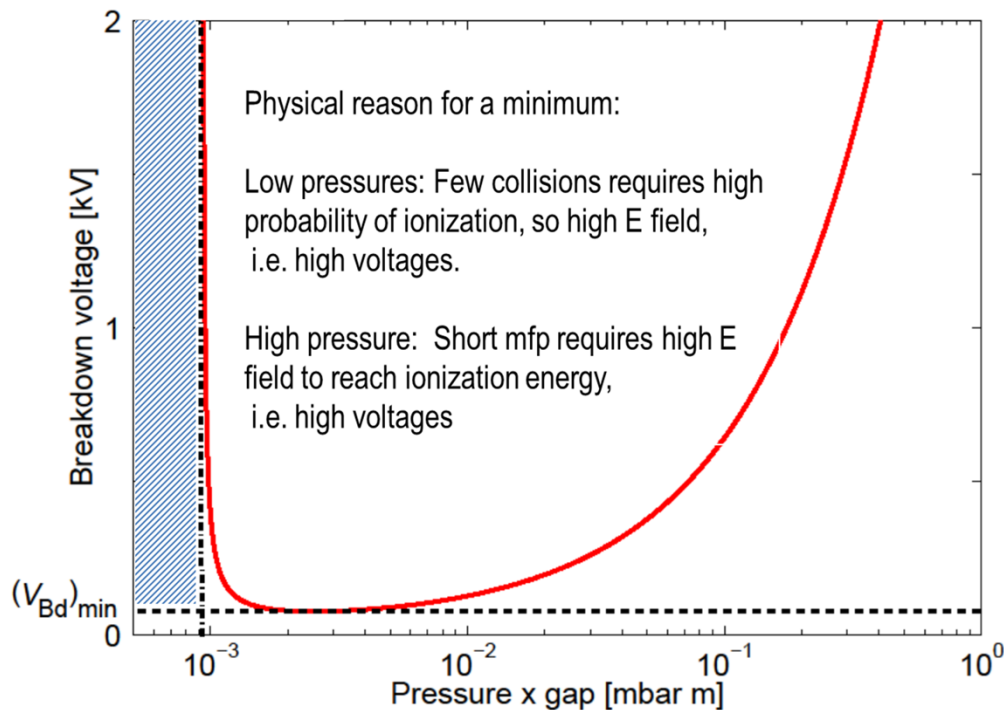
$$d/\lambda \propto p \cdot d$$

2. Electron collision energy:

$$eE\lambda = eV\lambda/d \propto 1/(p \cdot d)$$

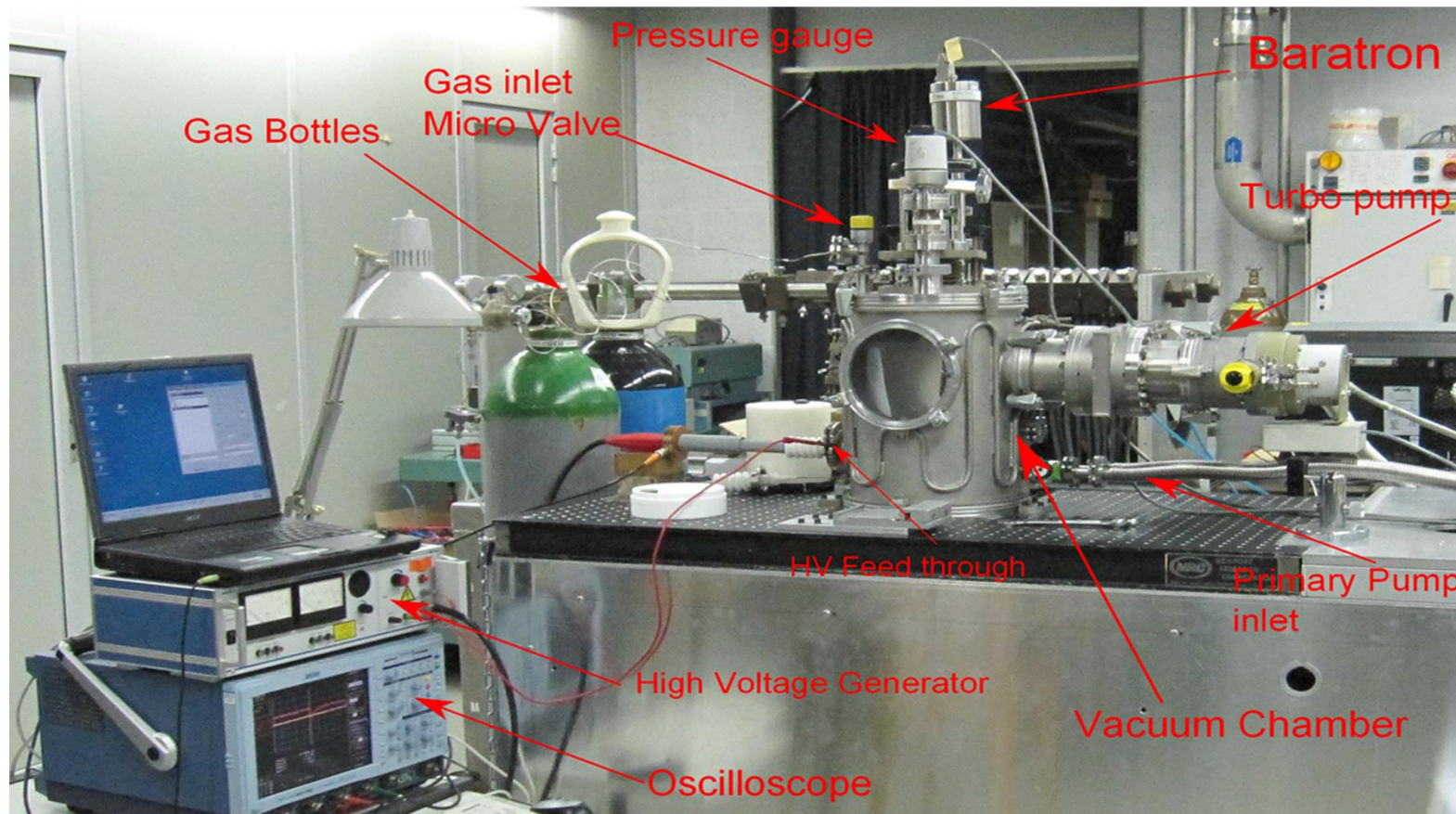
- The form of the curves depends on
 - α , which depends on the gas type
 - γ , which depends on the gas type and the electrode material

Paschen's law: DC breakdown between parallel plates

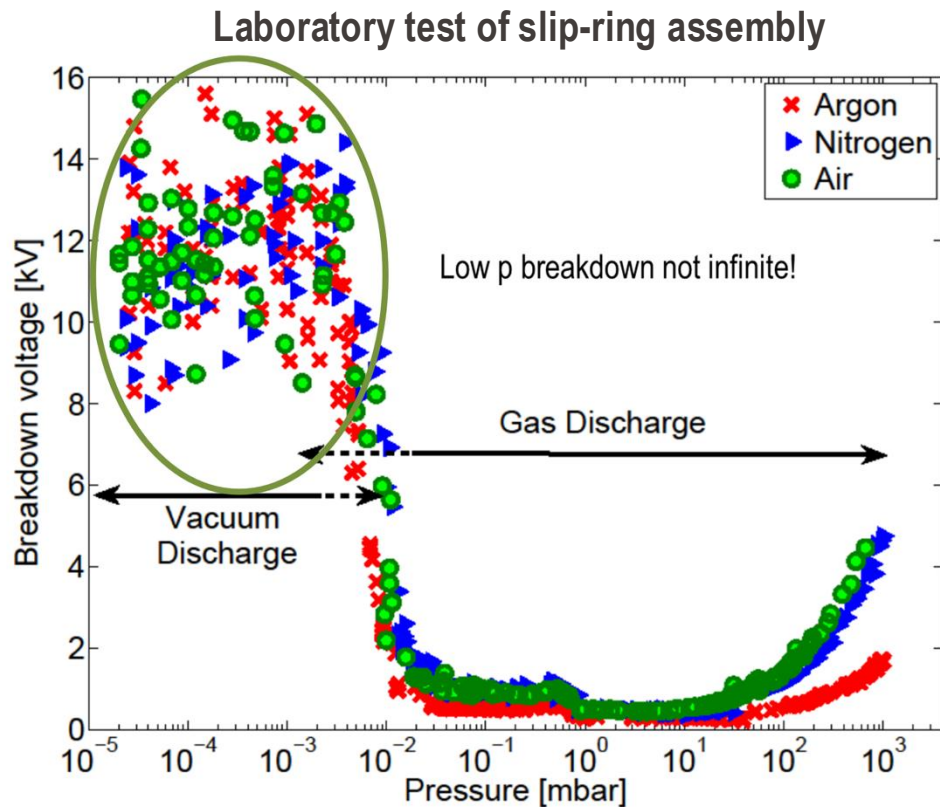


Breakdown measurements for real applications

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

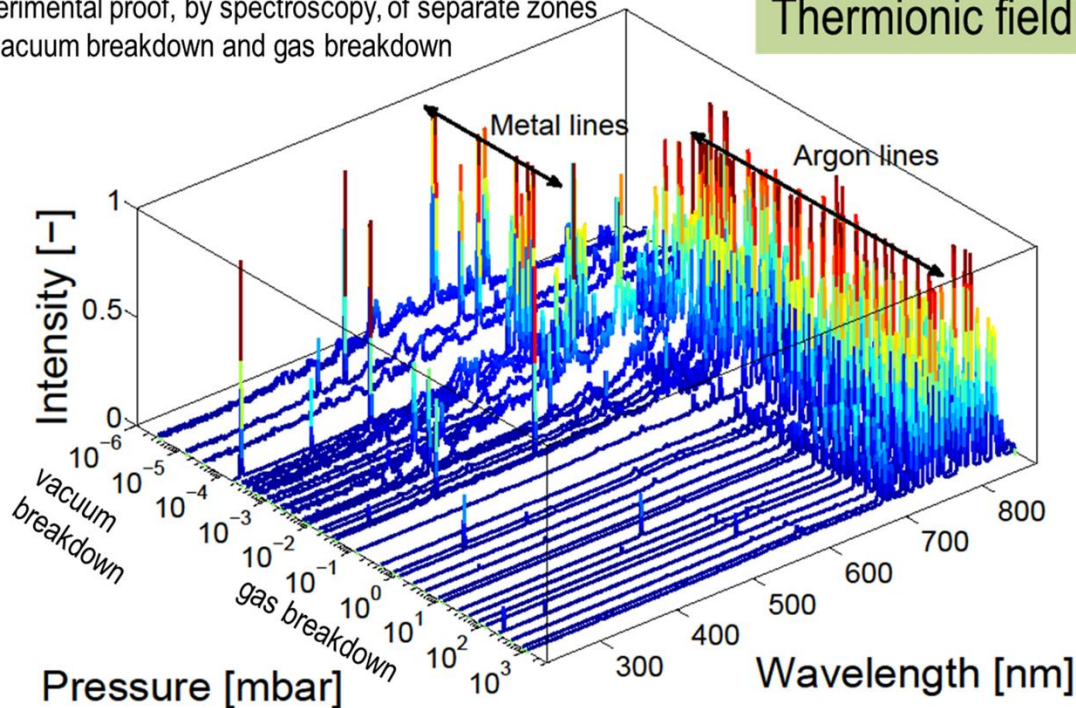


Breakdown measurements

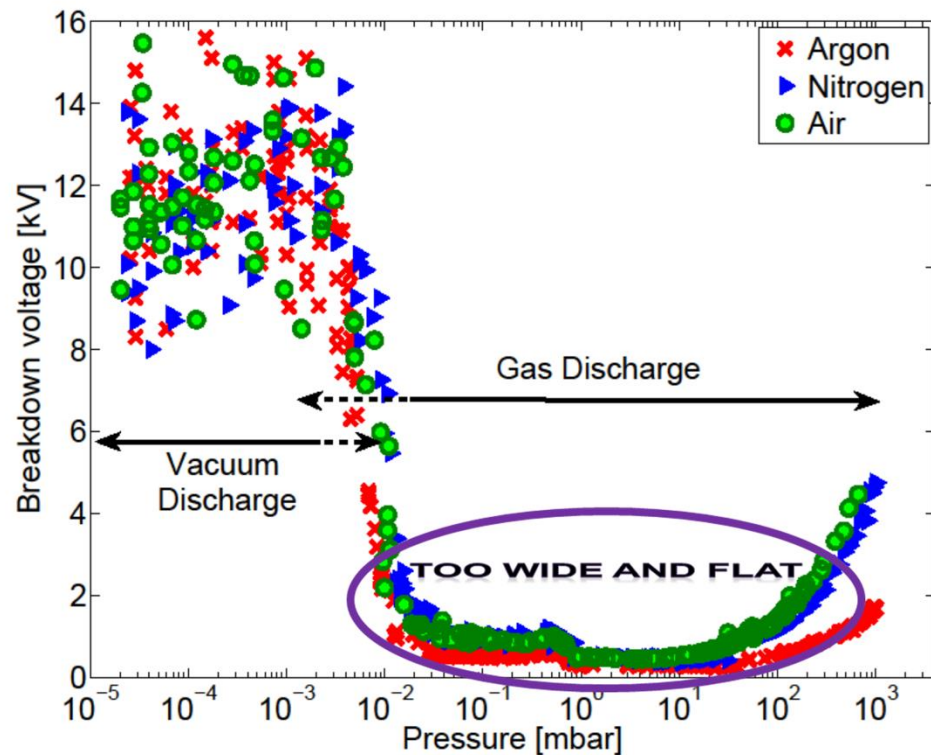


Experimental proof, by spectroscopy, of separate zones for vacuum breakdown and gas breakdown

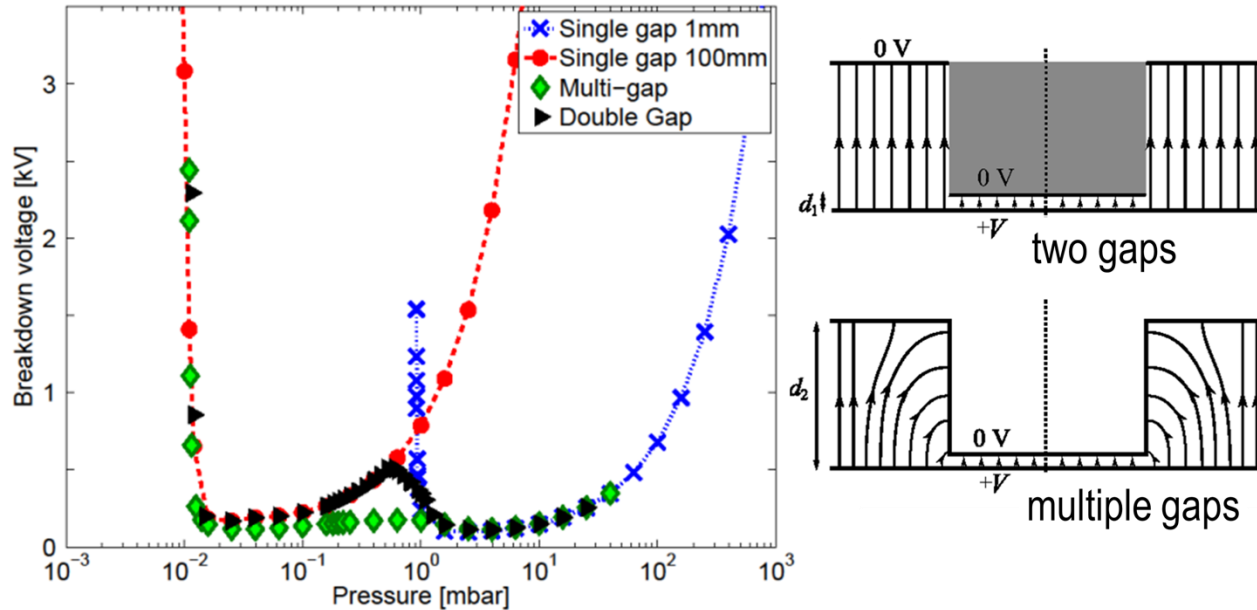
Thermionic field emission



Laboratory test of slip-ring assembly



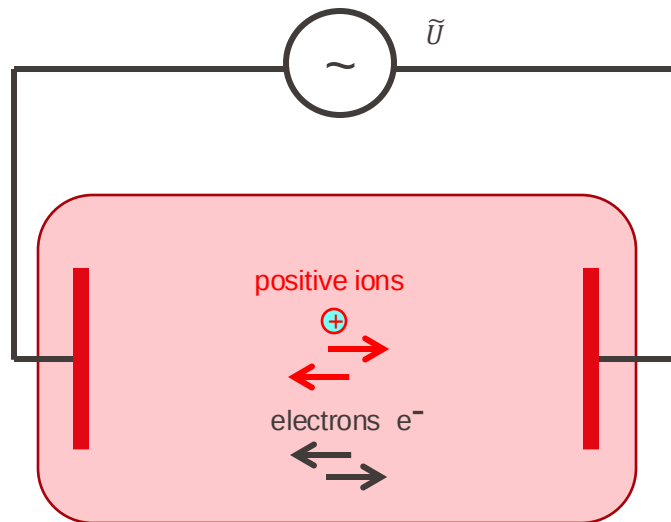
Breakdown numerical simulations



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

Other forms of breakdown: RF breakdown

- In oscillating fields the surface processes at the electrode/antenna become less important
- Electrons 'confined' in oscillating field keep ionising
- Ionisation source compensated by diffusive losses



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: $i = \frac{i_0 e^{\alpha d}}{1 - \gamma(e^{\alpha d} - 1)}$
- Breakdown criterion: $\gamma e^{\alpha d} = \gamma + 1$
- Townsend's first coefficient: $\alpha = A p e^{-\frac{B p}{E}}$
- Paschen's law for parallel plates: $V_B = \frac{B \cdot p d}{\ln(C \cdot p d)}$
- Vacuum and multi-gap breakdown