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# Methane conversion in homogeneous discharge at atmospheric pressure in Ar-CH<sub>4</sub> mixtures



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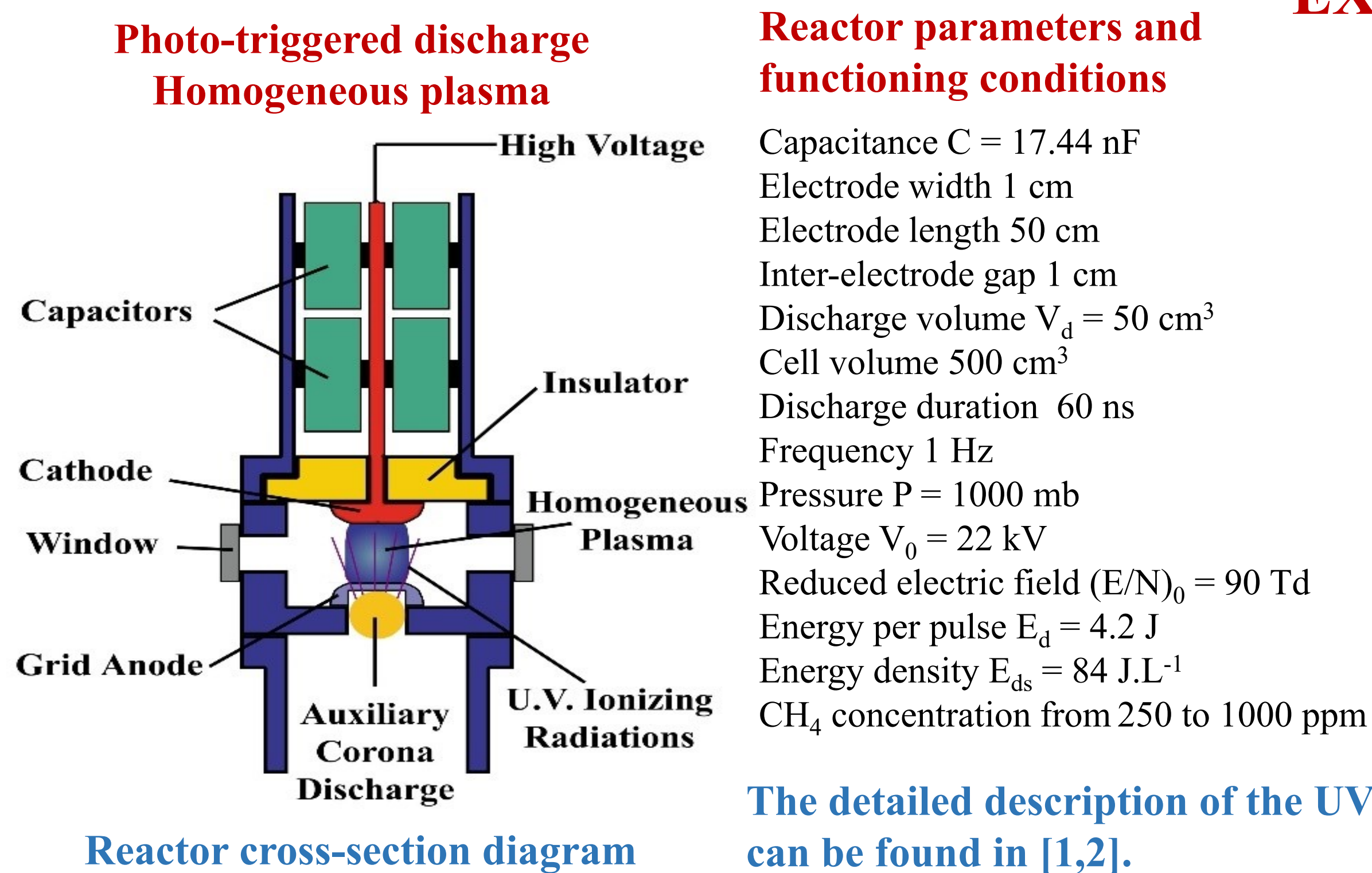
Université Paris-Saclay, CNRS, Laboratoire de Physique des Gaz et des Plasmas, 91405 Orsay, France

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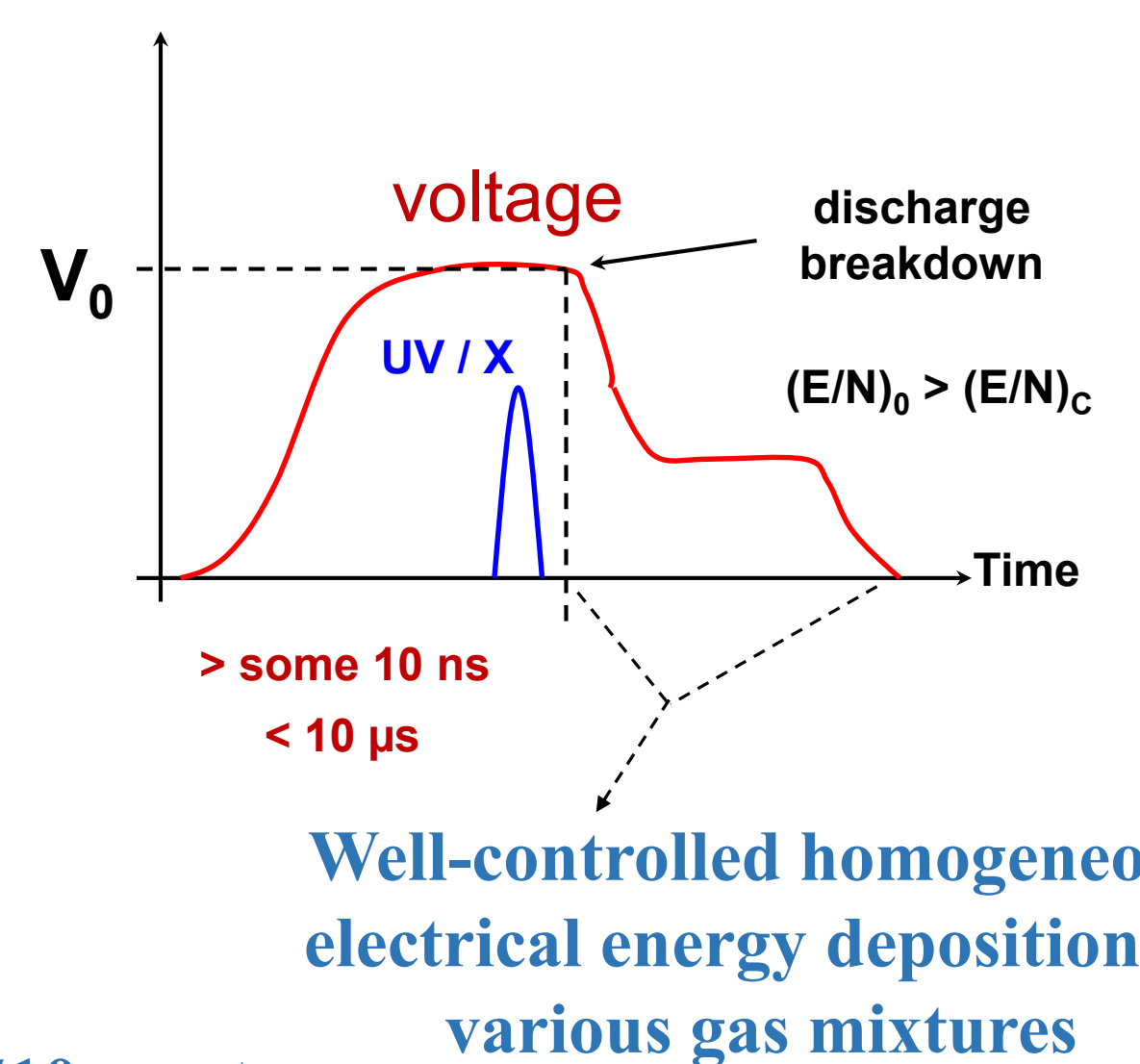


**AIM OF THE STUDY:** this work is our first step in the study of the physico-chemical processes involved in the conversion of methane by non-thermal plasmas in Ar-CH<sub>4</sub> mixtures. A UV pre-ionized photo-triggered discharge reactor is used, it allows to work with an homogeneous plasma, a uniform electric field and a controllable deposition of electric energy in the plasma even at atmospheric pressure. The moderate values of the reduced electric field E/N, associated with the preceding properties, allows a 0D self-consistent physical and chemical modelling, without restrictive hypothesis on the physics of the energy deposition. Initial methane concentrations are in the range 250-1000 ppm at atmospheric pressure, chromatographic diagnostics are used to identify and quantify CH<sub>4</sub> and by-products.

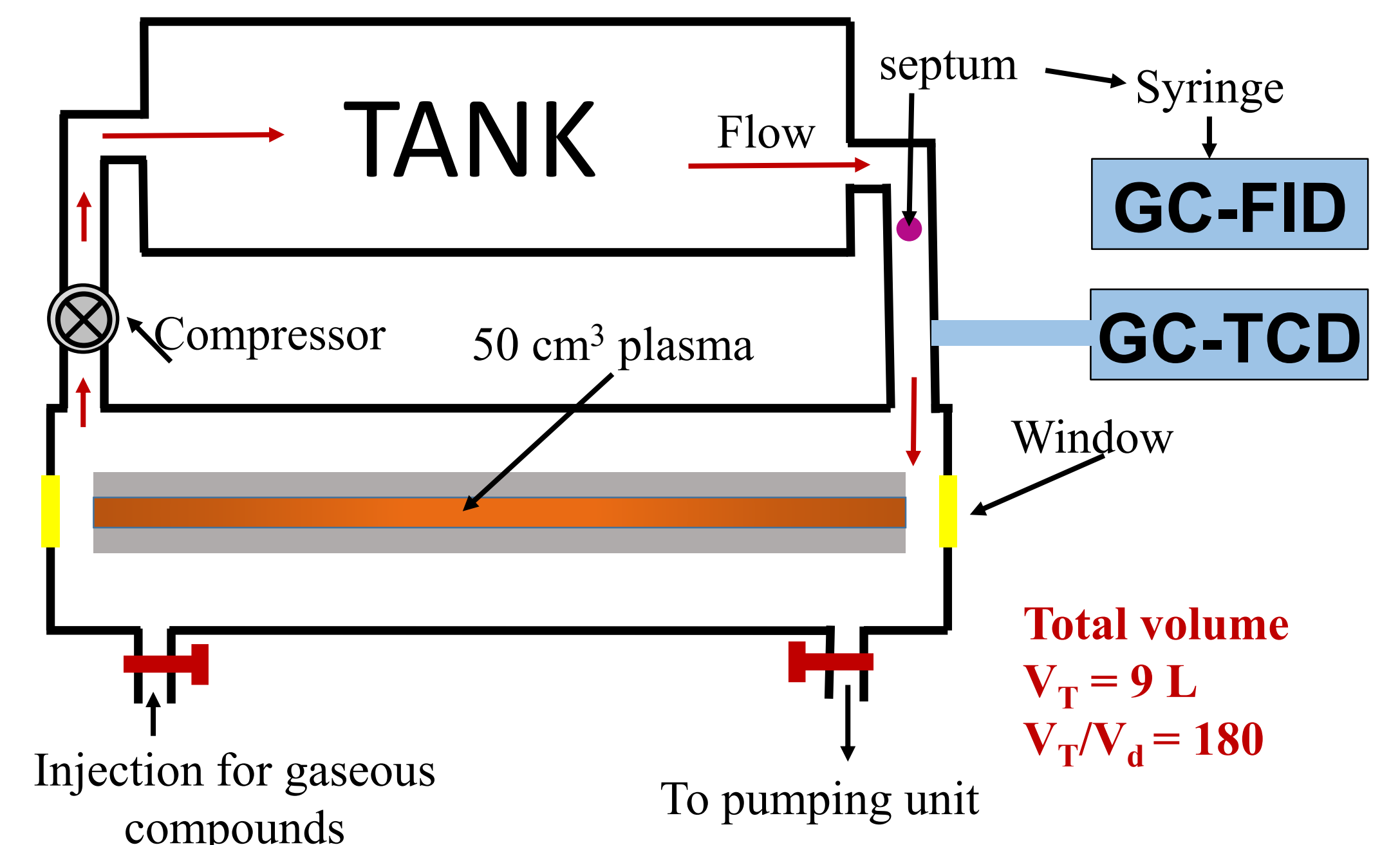
## EXPERIMENTAL SETUP



### General principle of operation

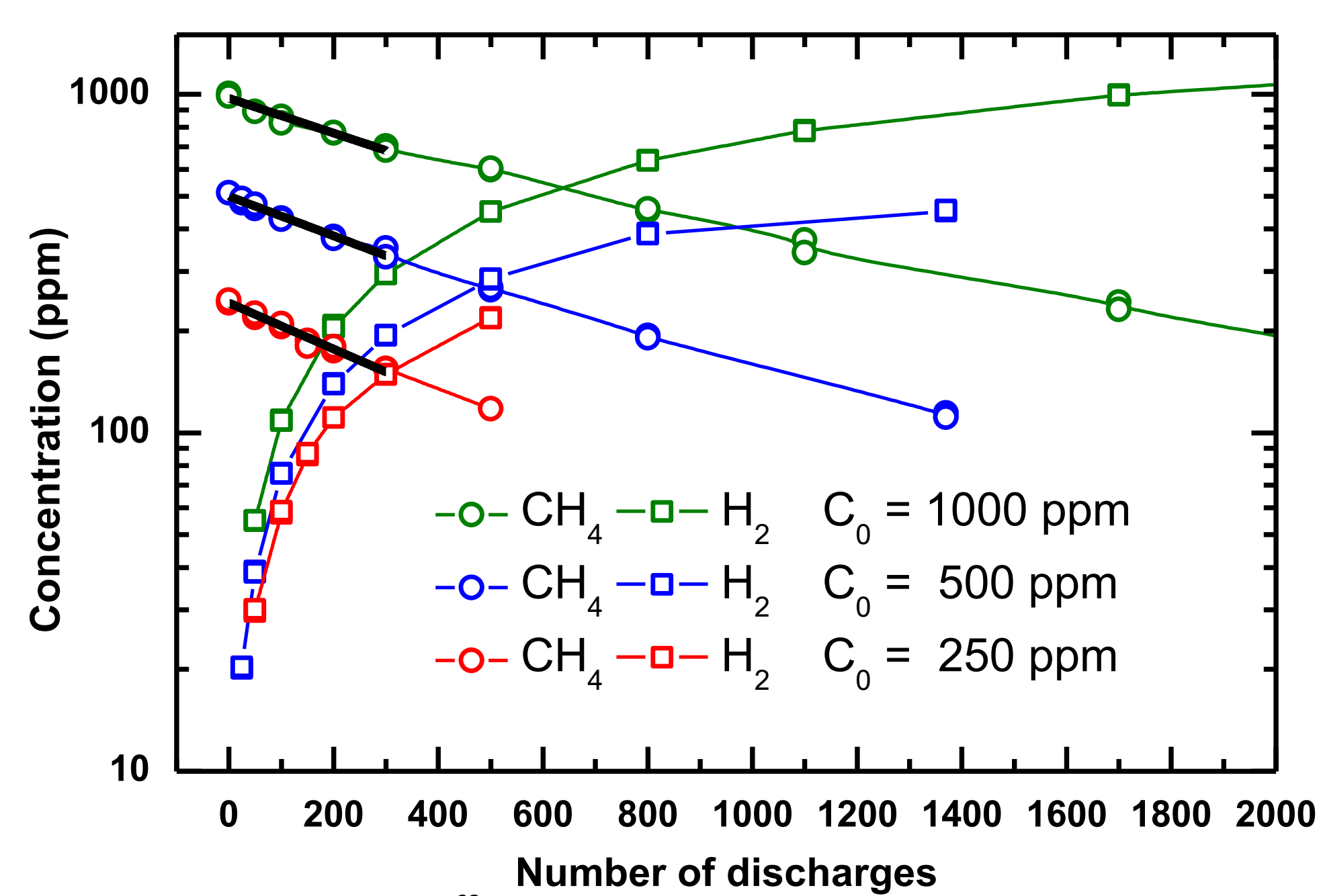


### Reactor arrangement and chemical diagnostics in the closed gas circuit loop.



## EXPERIMENTAL RESULTS

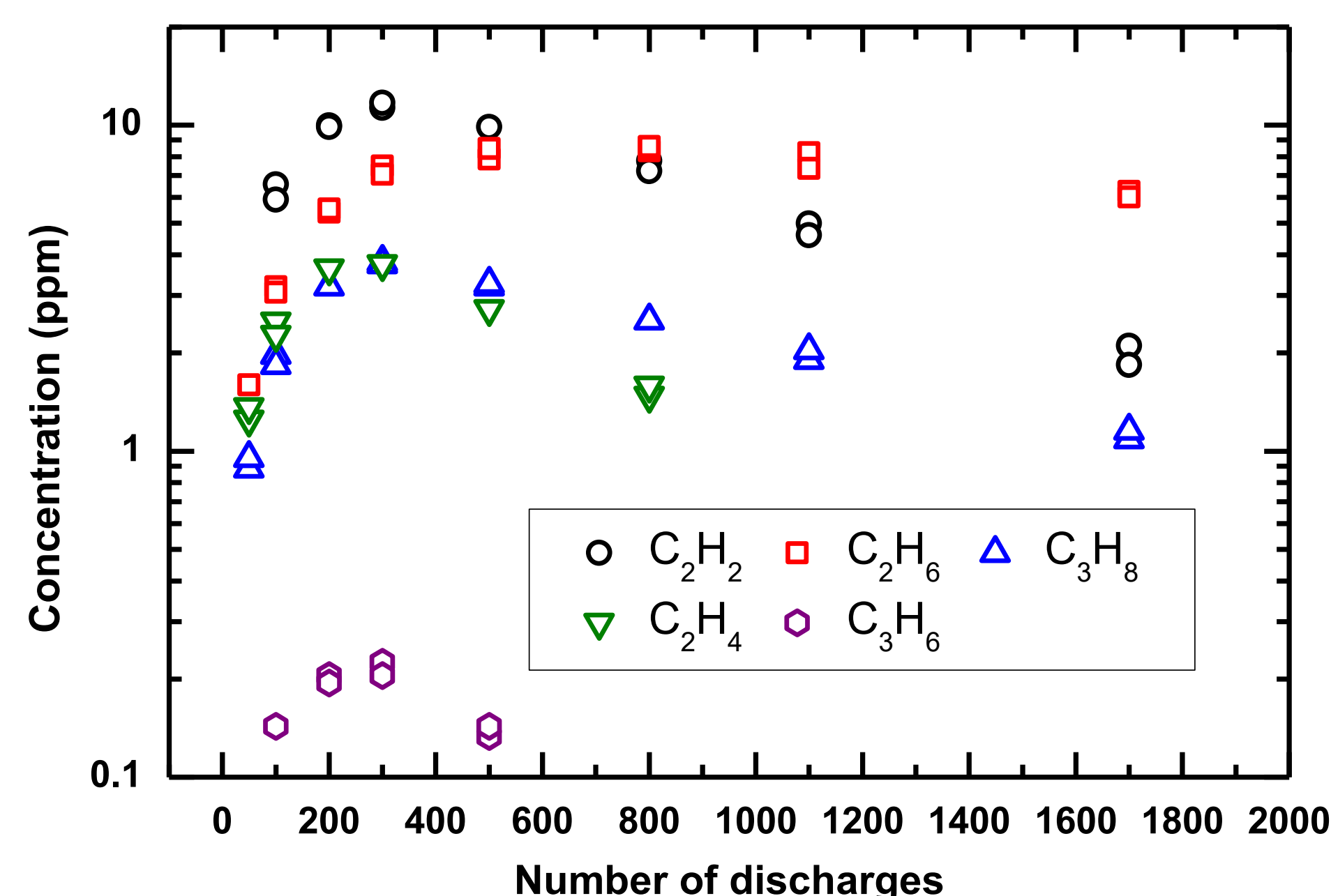
CH<sub>4</sub> and main by-products measurements in the gas circuit: H<sub>2</sub> with GC-TCD and hydrocarbons with GC-FID



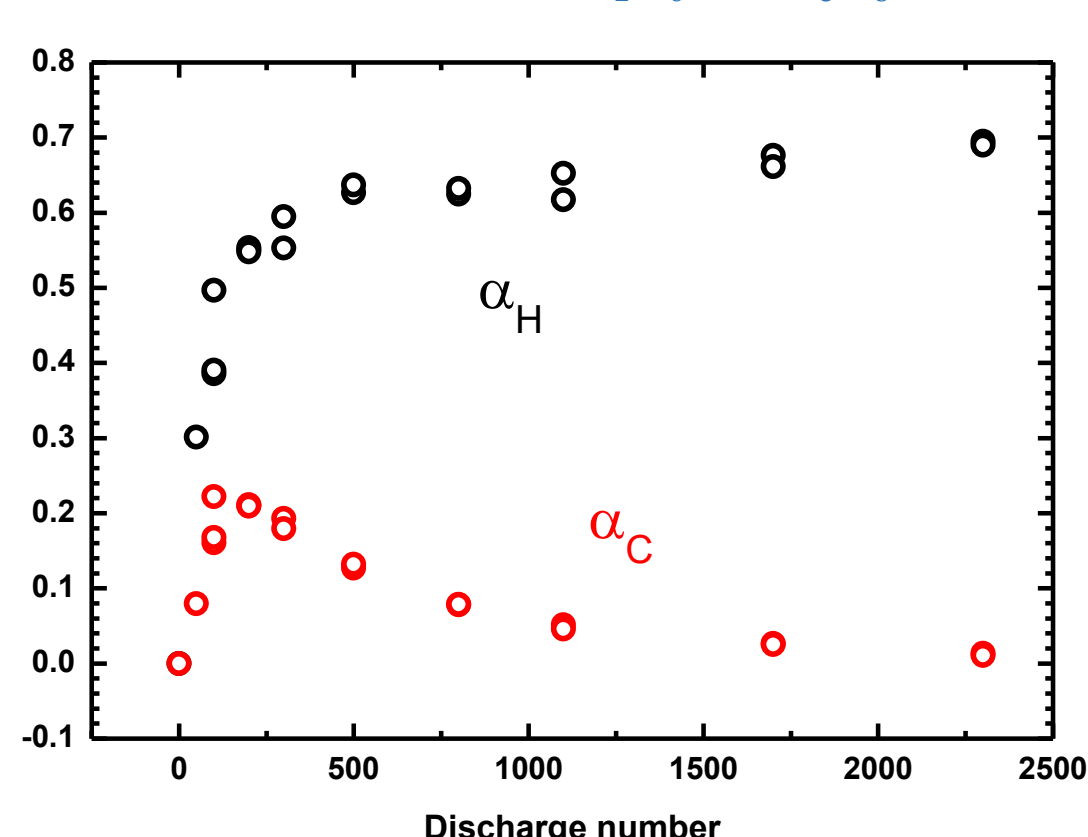
$$C_{CH_4} = C_0 \times \exp\left(-\frac{n}{N_c}\right)$$

The CH<sub>4</sub> evolution versus the number of discharges n is fitted with an exponential law (up to n=300) to evaluate the conversion in the first pulse in the gap. This value will be compared to the results given by the self-consistent 0D model of the discharge.

C <sub>0</sub> (ppm)	N <sub>c</sub>	E <sub>c</sub> (J.L <sup>-1</sup> )	C <sub>0</sub> -CH <sub>4</sub> (n=1) in the gap (ppm)
1000	844	394	213 (21%)
500	741	345	121 (24%)
250	638	298	70 (28%)



The maximum concentration of the measured by-products seems to be reached around 300 discharges. The concentration of unsaturated hydrocarbons C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> decreases faster than that of saturated hydrocarbons C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>.



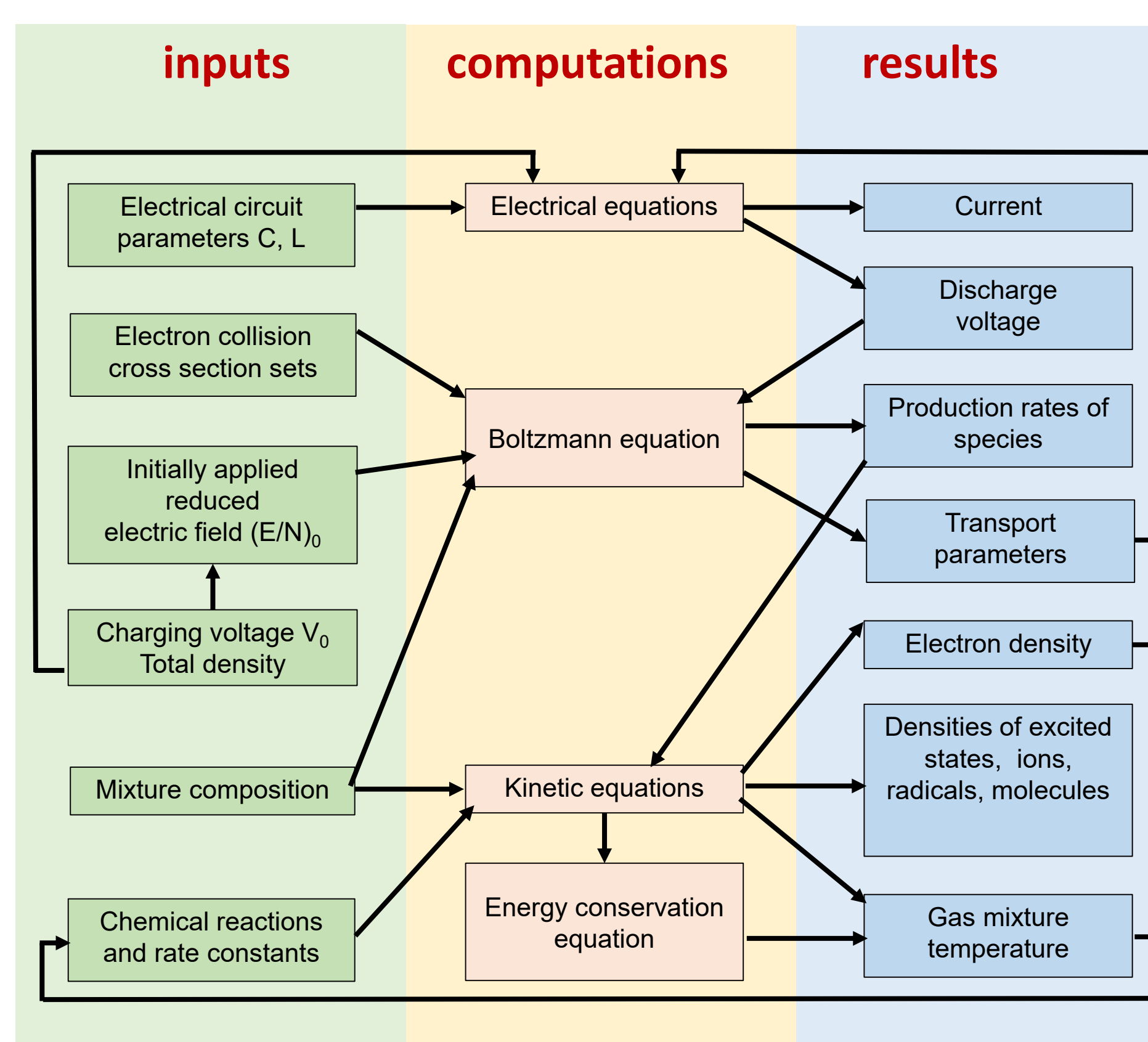
### C and H balances

$$\alpha_H = \frac{2[H_2] + 2[C_2H_2] + 4[C_2H_4] + 6[C_2H_6] + 6[C_3H_6] + 8[C_3H_8]}{4([CH_4]_0 - [CH_4])}$$

$$\alpha_C = \frac{2[C_2H_2] + 2[C_2H_4] + 2[C_2H_6] + 3[C_3H_6] + 3[C_3H_8]}{[CH_4]_0 - [CH_4]}$$

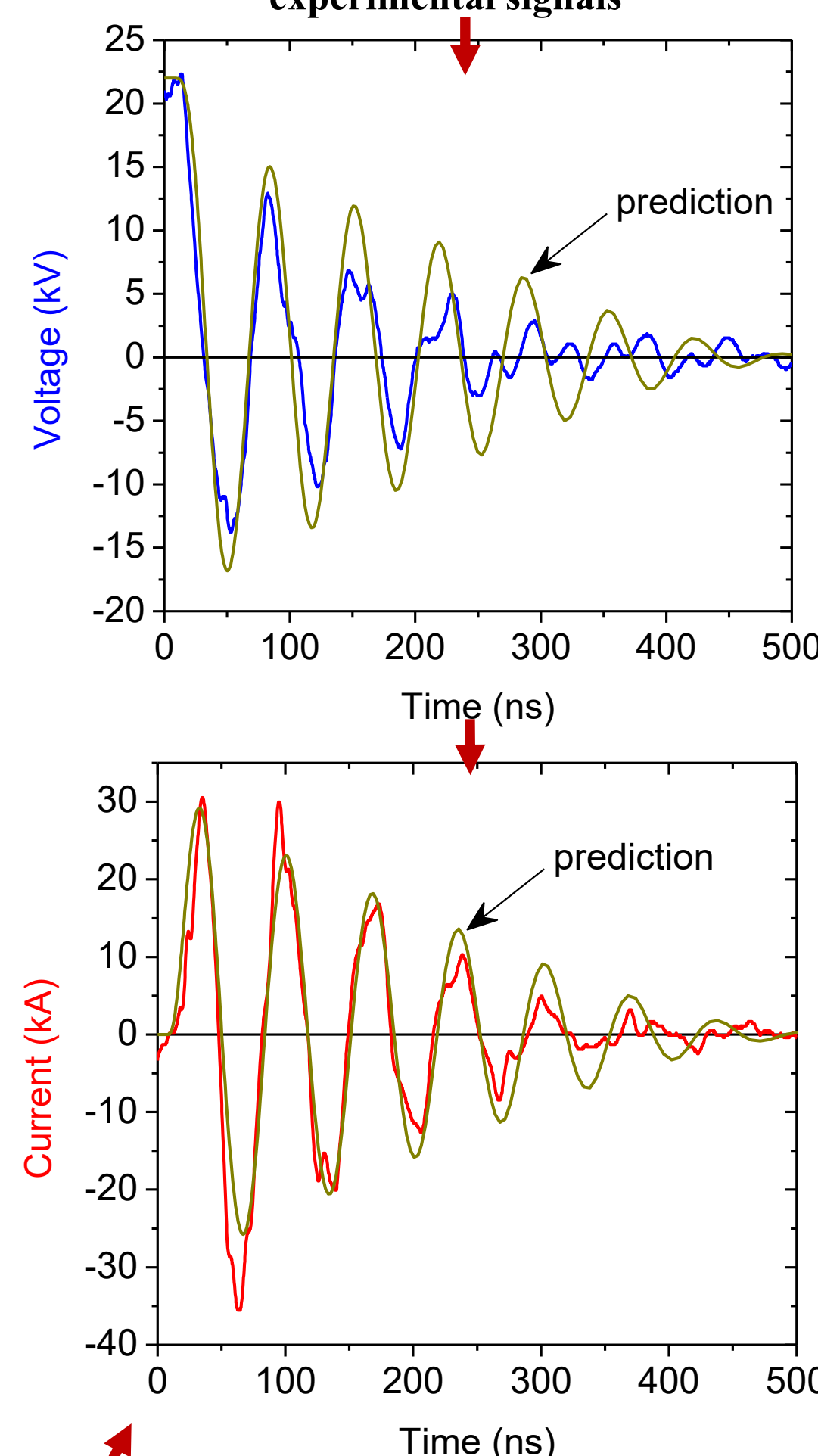
Concentration of detected carbon in by-products is very small compared to the converted methane. A lack of H is also observed to a lesser extent, suggesting formations of undetected heavier hydrocarbons and/or solid compounds.

## THE SELF-CONSISTENT 0D MODEL



Pure argon, P = 1 bar  
V<sub>0</sub> = 22 kV, (E/N)<sub>0</sub> = 90 Td

Comparison of calculated evolutions of voltage and current with the experimental signals

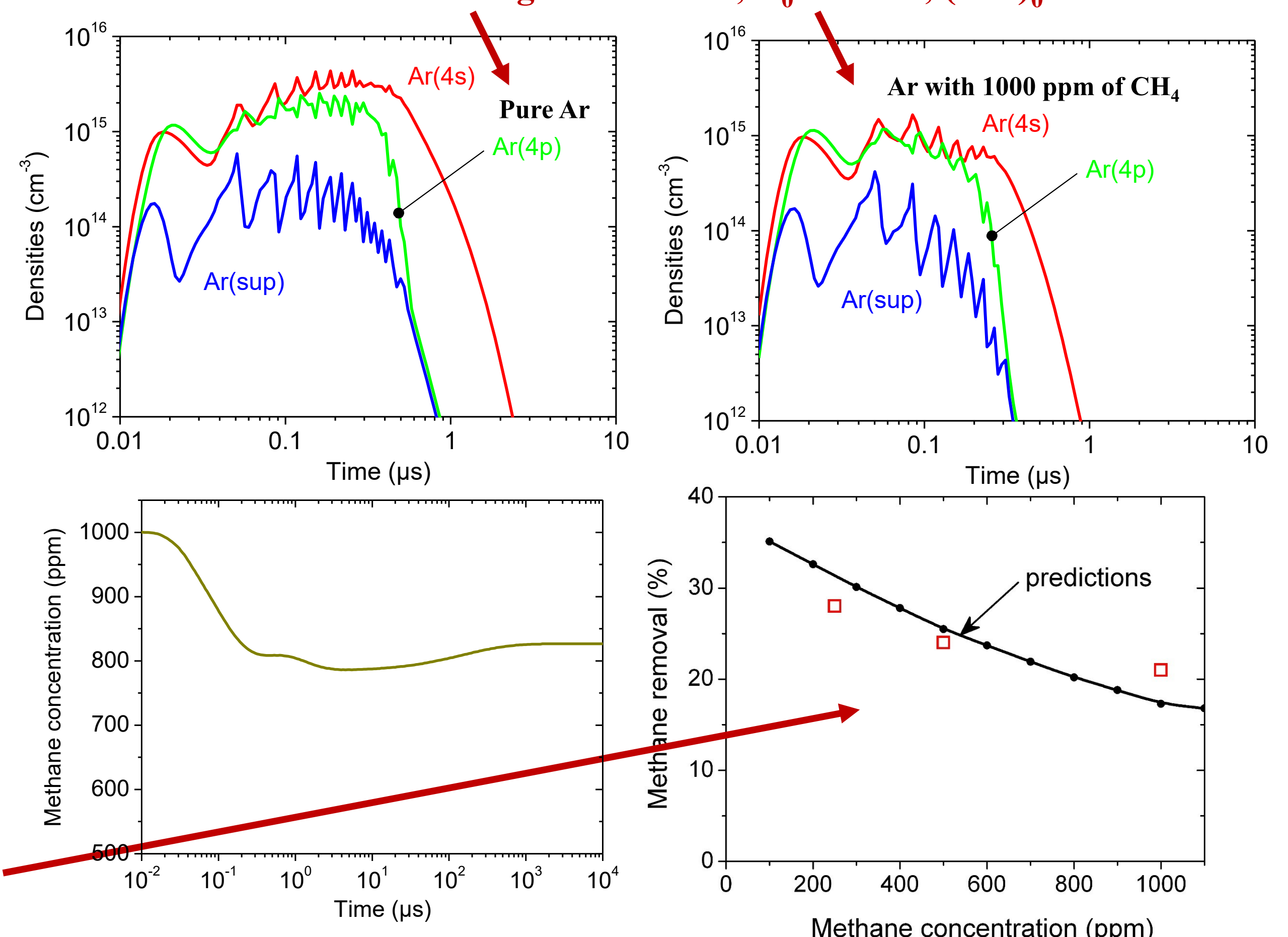


A good agreement is obtained between calculated and measured voltage and current. The agreement between calculated and measured CH<sub>4</sub> destruction in the gap during the first pulse is also satisfying, in spite of the simplicity of this first attempt in the modelling.

### Argon states clustering

Real states	Energies (eV)	Effective state	Energy (eV)
1s <sub>5</sub>	11.548	4s	11.652
1s <sub>4</sub>	11.623		
1s <sub>3</sub>	11.723		
1s <sub>2</sub>	11.827	4p	13.17
2p <sub>10</sub> ...	12.90...		
2p <sub>1</sub>	13.48		
all others	> 13.8	sup	14.5

### Influence of the methane concentration on the calculated evolutions of the radiative states of Argon. P = 1 bar, V<sub>0</sub> = 22 kV, (E/N)<sub>0</sub> = 90 Td.



### Simplified kinetics

**Electronic collisions**  
(LXCat database: V. Puech and BSR for Ar, M.-C. Borge for CH<sub>4</sub>)  
el + Ar : 4s, 4p, sup, Ar<sup>+</sup>  
el + 4s : 4p, Ar<sup>+</sup>  
el + 4p, sup : Ar<sup>+</sup>  
el + CH<sub>4</sub> : 2 vib. levels (0.16 eV and 0.36 eV)  
: dissociation CH<sub>3</sub> (10 eV)  
: ionisation CH<sub>4</sub><sup>+</sup> (12.98 eV)  
CH<sub>3</sub><sup>+</sup> (14.3 eV)  
CH<sub>2</sub><sup>+</sup> (15.1 eV)  
CH<sup>+</sup> (22 eV)  
H<sup>+</sup> (21.89 eV)

With production of H and H<sub>2</sub>  
Super elastic collisions (4s, 4p, sup, vib. CH<sub>4</sub>).

### Heavy particles

Pennings, charge transfers, excitation transfers  
excimer formation (Ar<sub>2</sub><sup>\*</sup>, Ar<sub>2</sub><sup>+</sup>), el-ion recombinations.

### Chemical kinetics

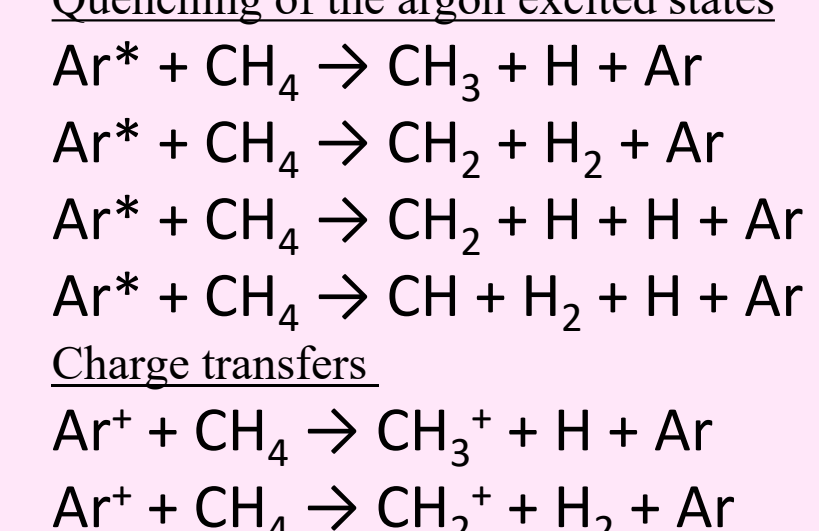
(NIST Database)  
H, CH, CH<sub>2</sub>, CH<sub>3</sub> → C<sub>x</sub>H<sub>y</sub> (X=2...6, Y=2...14).

### Radiative de-excitations

4p, sup, Ar<sub>2</sub><sup>\*</sup> (radiation trapping for 4s).

### Methane removal processes

Ref: P. Tosi et al., Int. J. Mass Spectrom. Ion Proc. 149/150 (1995) 345-353  
Quenching of the argon excited states



Open question: role of Ar<sub>2</sub><sup>\*</sup> and Ar<sub>2</sub><sup>+</sup> ?

## REFERENCES

- [1] N Moreau, S Pasquiers, N Blin-Simiand, L Magne, F Jorand, C Postel and J-R Vacher, J. Phys. D: Appl. Phys. **43** (2010) 285201 (14pp)
- [2] W Faider, S Pasquiers, N Blin-Simiand and L Magne, J. Phys. D: Appl. Phys. **46** (2013) 105202 (16pp)

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