SIMILARITY PRINCIPLES OF NON-ISOTHERMAL PLASMA CHEMICAL REACTORS

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Abstract

By modelling the non-isothermal positive column plasma the conditions of chemical similarity are developed within the frame of MICROSCOPIC and MACROSCOPIC KINETICS. Similar reactors are characterized by equal values of the relative concentrations of particles $x_i = n_i/n$; $n = \sum n_j$. This is the case with equal values of the reduced summary effective source term $\tau_0 \widehat{S_i}/n$ (τ_0: residence time in the active zone of the reactor; $S_i = G_i - L_i$: gain minus loss of particles i per units of time and volume, respectively). On this $\widehat{S_i}$ is related to the combination of the active and passive zone. Under selected conditions $\tau_0 \widehat{S_i}/n$ can be expressed as a function of a dimensionless REACTOR PARAMETER $R = \tau_0\, P/pV$ (P: power input; p, V: gas pressure and volume of the active zone). Then we have $x_i = x_i(R)$ and similar reactors correspond to equal R. Large values of R result in quasi-equilibrium states, which can be described by an electronically modified mass action law.

Introduction

Although sealing concepts in plasma physics (e.g. for fusion devices or thermal plasmatrons) are well known, the principles of plasma chemical similarity of non-equilibrium reactors seems to be underdeveloped. In the following we discuss some aspects of this similarity for the reactive plasma of the positive column of glow discharges. The combination of plasma equations (especially the BOLTZMANN Equation of electrons) with the transport equation of chemical species

$$\partial n_i/\partial t + div\ \vec{v}\ n_i - div(D_i\ grad\ n_i) - S_i = 0 \qquad (1)$$

results in the distributions $n_i(\vec{r}, t)$ for similar reactor conditions. Within the frame of the B-invariant similarity principle [1] identical $x_i(\vec{r}/r_0, t/\tau_0)$ requires the correspondence of nr_0, $I/r_0, \tau_0\ n$ for similar reactors. In this case the rate S_i is limited to selected reactions (e.g. two-body collisions). In practice not the whole distributions x_i in space and time of all species (stable and unstable one) are of interest; sufficient is the knowledge of only stable products at the output of reactors with long passive zones [2]. To prove plasma chemical similarity under these restricted conditions an adequate simplified reactor model is usefull.

Reactor Model

Indispensable is the subdivision of the flow reactor in two different zones: Active Zone (AZ, plasma region) and Passive Zone (PZ, afterglow). Fig. 1 shows the both zones for an one-dimensional, steady-state flow reactor after averaging n_i, taking into account convective in-and outflow only. This model corresponds to the so-called Back Mixing Model. Within the approximations mentioned Equ.(1)

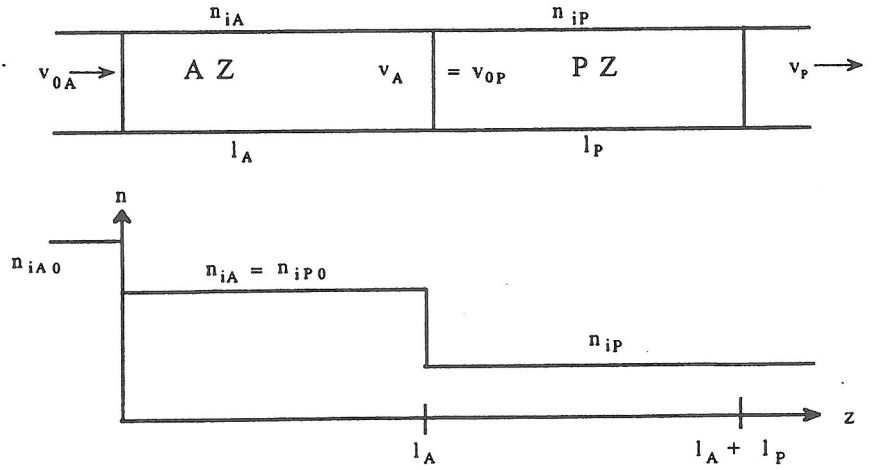

Figure 1: Reactor Model

results in:

$$AZ: \qquad l_A\, S_{iA} = v_A\, n_{iA} - v_{0A}\, n_{iA0}$$
$$PZ: \qquad l_P\, S_{iP} = v_P\, n_{iP} - v_{0P}\, n_{iP0}$$

Because of $v_A\, n_{iA} = v_{0P}\, n_{iP0}$ we get

$$AZ + PZ: \qquad l_A\, S_{iA} + l_P\, S_{iP} = v_P\, n_{iP} - v_{0A}\, n_{iA0}$$

Introducing a summary effective source term

$$\widehat{S_i} = S_{iA} + \lim_{l_P \to \infty} (l_P/l_A)\, S_{iP}$$

the balance equation for the output values x_i of stable products reads as follows:

$$\tau_0\, \widehat{S_i}\, /\, n = v\, x_i/v_0 - x_{i0} \quad with \quad v \sum m_j x_j = v_0 \sum m_j x_{j0} \qquad (2)$$

According to that: Two reactors are similar (i.e. equal input values x_{i0} result in equal x_i) if the reduced summary effective source terms $\tau_0\, \widehat{S_i}/n$ agree in both cases.

Example of Demonstration

For illustration we analyse a simple microscopic reaction scheme, including three species A_1, A_2, A_m and electrons e and two rate coefficients k_1, k_2.

$$A_{1,2} + e \longrightarrow A_m + e$$
$$A_{1,2} + A_m \longrightarrow A_1 + A_2$$

The MICROSCOPIC KINETICS gives:

$$\tau_0 \, \widehat{S_1} \, / \, n = k_2 n \; x_{2A} \; \tau_0 \; x_{mA} - k_1 n \; x_{1A} \; \tau_0 x_e + x_2 \; x_{mA} \qquad (3)$$

$$x_1 = \frac{x_{mA} + x_{1A}}{x_{mA} + 1} \; ; \qquad x_2 = 1 - x_1$$

$$x_{mA} \approx \frac{k_1 n \; \tau_0 x_e}{1 + \; k_1 n \; \tau_0 x_e + k_2 n \; \tau_0}; \qquad x_{1A} = \frac{k_2 n \; \tau_0 \; x_{mA}(1 - x_{mA}) + x_{10}}{k_2 n \; \tau_0 \; x_{mA} + k_1 n \; \tau_0 x_e + 1}$$

The rather complicated expression $x_1 = x_1(n\tau_0, n\tau_0 x_e)$ reflects in the critical cases $x_e \to \infty$ and $\tau_0 \to \infty, x_e \to 0$ equal values of the quasi-equilibrium states CECD and CEEC $x_1^\infty = x_1^0 = 1/2$ (for the definition of quasi-equilibrium see [2]). The MACROSCOPIC KINETICS (see [3]) gives for the gross reaction between the stable products

$$A_1 + e \rightleftharpoons A_2 + e \quad \text{rate coefficient} \quad k$$

$$\tau_0 \, S_1/n = kn\tau_0 x_e(x_2 - x_1); \qquad x_1 = \frac{kn \; \tau_0 x_e + x_{10}}{1 + 2kn \; \tau_0 x_e} \qquad (4)$$

This much simpler function contains the expression $n\tau_0 x_e$ alone: $x_1 = x_1(n\tau_0 x_e)$. Of special interest is the comparision between the results of microscopic and macroscopic kinetics. Fig. 2 shows that within the whole operation region of $\tau_0 x_e$ the differences remain small (percent). The model of MACROSCOPIC KINETICS is an excellent approximation. The output values are given by KINETIC CURVES $x_i = x_i(n\tau_0 x_e)$, containing the parameter $n\tau_0 x_e$ alone which appoints plasma chemical similarity in this case. The role of $\tau_0 x_e$ is demonstrated by measurements of the ozone synthesis in flowing oxygen (Figs. 3 and 4).

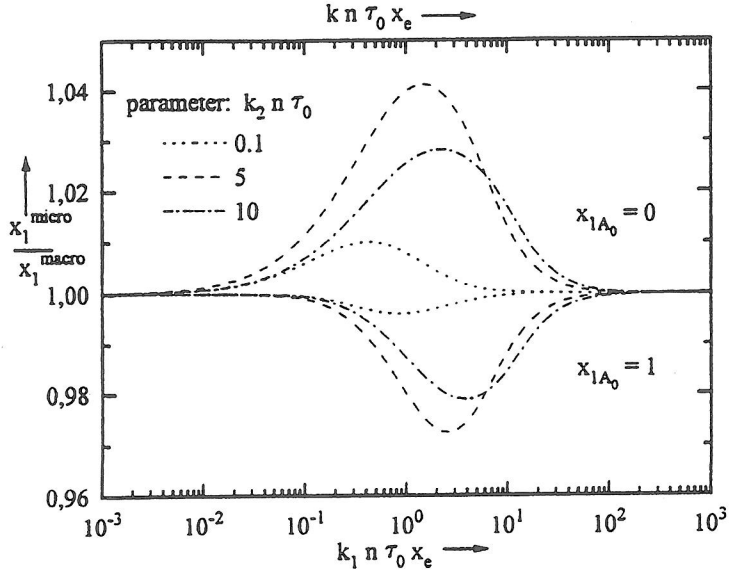

Figure 2: Comparison of the micro -and macroscopic description

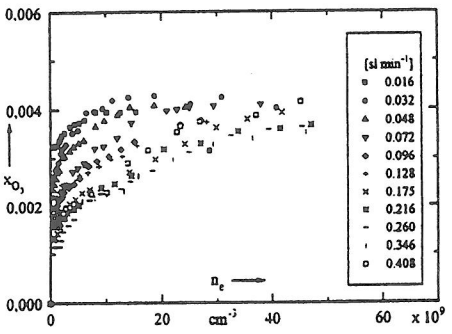

Figure 3: Relative ozone concentration in dependence on n_e (parameter τ_0)

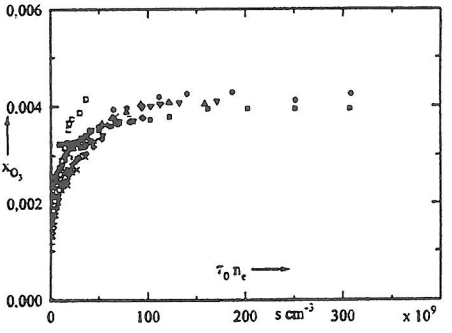

Figure 4: Relative ozone concentration in dependence on $\tau_0 n_e$

The Dimensionless Reactor Parameter R

In the case of different rate coefficient k^+, k^-, forward and backward reaction respectively, the source term (4) becomes:

$$\tau_0 \, S_1 \, / \, n = \frac{n \, \tau_0 x_e \, (k^- - (k^- + k^+) \, x_{10})}{1 + (k^- + k^+) \, n \, \tau_0 x_e} \qquad (5)$$

Generally k^+, k^- are functions of n, T_G, T_e . At high values $T_e \geq 1eV$ the rate coefficients are widely independent of T_e [2]. In many cases (e.g. with two-body collisions only) the dependence on n disappeared, too. With $T_G = const$, which is a general premise for plasma chemical similarity, no variation of k^+, k^- occurs and similarity exists with identical values $n\tau_0 x_e = \tau_0 n_e$, as already mentioned. The electron concentration in the active zone of the reactor is given by:

$$n_e = (aP)/(pV); \qquad a = a(E/n)$$

With $a \approx const$ (this requires $E/n \approx const$) we get $n\tau_0 x_e = \tau_0 n_e \sim R = \tau_0 P/pV$ and plasma chemical similarity is connected with identical values of the reactor parameter R. At small $R \to 0$ the source term (5) becomes $\tau_0 \, S_1 \, / \, n \sim R$. Large $R \to \infty$ results in $\tau_0 \, S_1 \, / \, n \to const$ and determines the quasi-equilibrium state

$$x_1 \to x_1^\infty = k^-/(k^- + k^+) \qquad or \qquad x_1^\infty / x_2^\infty = k^-/k^+ = K(T_G)$$

which can be interpreted as an electronically modified mass action law. Exact the same behaviour shows the microphysical expression (3). Regarding the physical meaning one sees: The parameter R is the energy invested per particle during its flow through the active zone in relation to the thermal energy kT.

Comparison with Experimental Results

The applicability of the parameter R could be already proved for different reaction mixtures. Figs. 5 and 6 show an example , using measurements [4] of the plasma chemical conversion of CH_4 (hf discharge; Ar +1%CH_4). By introducing R the different curves of Fig. 5 appearently converge.

List of Symbols

E: electric field strength, I: current, r_0: radius of the positive column
n: total particle concentration, p: gas pressure, P: electrical power, invested in the active zone, T_G, T_e: temperature of gas and electrons, respectively , V: volume of the active zone, v_e: electron drift velocity , $x_e = n_e/n$: degree of ionization, τ_0: residence time of particles in the active zone

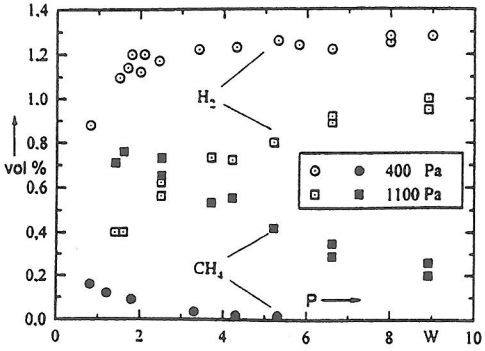

Figure 5: Concentration of H_2 and CH_4 in dependence on the power P [4]

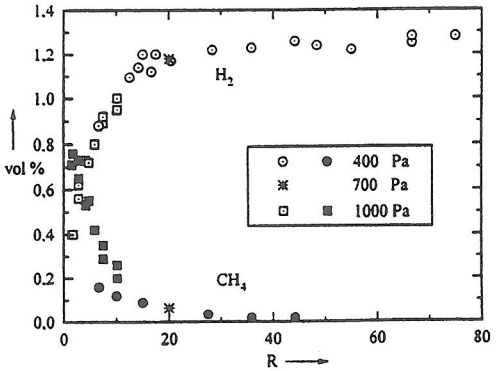

Figure 6: Concentration of H_2 and CH_4 as in Fig. 5 but in dependence on the reactor parameter R

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