THE COMBINED THERMAL AND RF-PLASMA ACTIVATION OF CHEMICAL REACTIONS IN THE MODEL-SYSTEM H_2 / I_2 / HI

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Abstract

The formation of the so called chemical quasi-equilibrium of electronic catalysis (CEEC) was investigated for the model system hydrogen / iodine / hydrogen iodide in rf-discharges in closed quartz glass tubes at different external gas temperatures. This equilibrium is characterized by the independence of the composition of stable reaction products (H_2, I_2, HI) on the ionization degree at vanishing concentration of electrons in the closed reactor. Especially the reversible transition was studied from the thermal equilibrium to this quasi-equilibrium . A simple kinetic model, including 21 reaction channels between the molecular and atomic components as well as selected ionic species, describes sufficently the plateau of the quasi-equilibrium. It reflects qualitatively the detected dependence on the gas temperature. The analysis of the reaction mechanism showed, that the quasi-equilibrium composition is controlled by only 4 reaction channels.

Introduction

Under non-isothermal conditions the experimental analysis of different plasma chemical conversions showed the occurence of two selected states of the stable reaction products which could be interpreted as chemical quasi-equilibria of the reactor [1] [2]. These quasi-equilibria characterize the limit situations of the reactor operation at low power input (in the closed system) and high power input, which includes the limits $n_e \to 0$ and $n_e \to \infty$, respectively (n_e: concentration of plasma electrons). They were qualified as [1]: Chemical Equilibrium of Electronic Catalysis (CEEC) and Chemical Equilibrium of Complete Decomposition (CECD) and are the base for the global description of non-isothermal reactors by the method of macroscopic kinetics. The investigations in the system hydrogen / iodine / hydrogen iodide mainly were suggested, because the thermal mechanism of the HJ-formation is relatively well known [4] [5]. Furthermore the thermal equilibrium state, estimated by the Mass Action Law (MAL), arrives already at temperatures below $600°C$ compositions, where the concentration values of the stable components $n_{H_2} = n_{I_2}$ as well as of n_{HI} have the same order of magnitude. Therefore this system was especially suitable to investigate the complex situation, characterized by thermal and plasma initiated chemical reactions and resulting in reversible transitions between the different Chemical Quasi-Equilibria and the thermal equilibrium. The main interest was aimed at the question, in which manner the thermal equilibrium is influenced by small concentrations of hot electrons, causing the CEEC.

Experimental

The experimental setup is shown in the parts of Fig. 1. The discharges operated in closed quartz tube reactors T, which were prepared under high vacuum conditions. The tubes were filled with defined input gas mixtures of iodine and hydrogen (sometimes in combination with an inert He puffer gas). The discharge tube could be located in a thermostat to externally regulate the gas temperature up to $600°C$ (Fig. 1, upper part). Vanishing ionization degrees were realized by the excitation of the mixtures in a very faint TESLA spark discharge. Higher ionization degrees were produced in capacitively coupled rf discharges (frequency: $450kHz$ ... $650kHz$). In this case the particle number density of electrons was determined by the microwave cavity method (Fig. 1, lower part). The microwave signal from the generator M was coupled into the resonator cavity R by the variable attenuator D, slotted waveguide W using inductive probe P. The microwave signal, decoupled by the inductive probe, was analyzed by the voltmeter V and oscilloscope O.
The experimental analysis of the stable reaction products was performed by absorption spectroscopy of iodine at $\lambda = 480nm$ (cross section from [3]) at the assumption of equal amounts of the hydrogen and iodine component. The line was emitted by a Cd-lamp L and registrated by the SEM S of a monochromator (lock-in-technique). After the plasma chemical synthesis of HI these molecules could be fully decomposed into H_2 and I_2 by the uv radiation of a mercury lamp UV. Therefore it was possible to generate a reversible overall chemical process.

The Kinetic Model

To understand the formation of the CEEC as well as the transition to the thermal equilibrium a simple kinetic model for the closed reactor was studied. The ionization degree of the plasma and the gas temperature are input parameters, estimated by experiments. The calculations were performed for time and space

Species incorporated	$H,\ I,\ I^-,\ e$ $H_2,\ I_2,\ HI,\ H_2I$	rate coefficients k_i in cm^3/s, γ_i in cm^6/s, α_i in s^{-1}
Electronic 1.	$H_2 + e \xrightarrow{k_1} H + H + e$	$k_1(E/N)\ (10^{-10})$
Processes 2.	$I_2 + e \xrightarrow{k_2} I + I^-$	$k_2(E/N)\ (10^{-9})$
3.	$HI + e \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H + I^-$	$k_3(E/n)\ (10^{-8})$
		$k_{-3}(E/n)\ (3\ 10^{-10})$
4.	$H_2I + e \xrightarrow{k_4} H_2 + I + e$	$k_4(E/N)\ (10^{-10})$
5.	$I^- + e \xrightarrow{k_5} I + 2\ e$	$k_5(E/N)\ (10^{-8})$
Thermal 6.	$I^- + M \xrightarrow{k_6} I + M + e$	$k_6 = 10^{-14}$
Reactions 7.	$I + I^- + M \xrightarrow{\gamma_7} I_2 + M + e$	$\gamma_7 = 2.3\ 10^{-30},\ M = I_2$
8.	$I + wall \xrightarrow{\alpha_8} 0.5\ I_2$	$\alpha_8 = \epsilon \bar{v}_I / 2r_0,\ \epsilon = 10^{-4}$
9.	$H + wall \xrightarrow{\alpha_9} 0.5\ H_2$	$\alpha_9 = \epsilon \bar{v}_H / 2r_0,\ \epsilon = 10^{-4}$
10.	$HI + I \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} H + I_2$	$k_{10} = 9.1\ 10^{-9} T^{0.5} exp(-18041/T)$
		$k_{-10} = 6.6\ 10^{-10} exp(-20/T)$
11.	$HI + H \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} I + H_2$	$k_{11} = 7.4\ 10^{-11} exp(-290/T)$
		$k_{-11} = 5.9\ 10^{-9} T^{0.5} exp(-16529/T)$
12.	$I + I + H_2 \underset{k_{-12}}{\overset{\gamma_{12}}{\rightleftharpoons}} H_2I + I$	$\gamma_{12} = 1.3\ 10^{-32},\ k_{-12} = 4.3\ 10^{-10}$
13.	$H_2I + I \xrightarrow{k_{13}} 2\ HJ$	$k_{13} = 8.8\ 10^{-14}$
14.	$I_2 + M \underset{\gamma_{-14}}{\overset{k_{14}}{\rightleftharpoons}} I + I + M$	$k_{14} = 5.3\ 10^{-4} T^{-1.8} exp(-17910/T)$
		$\gamma_{-14} = 2.3\ 10^{-30}\ (M = I_2)$
15.	$H_2 + M \underset{\gamma_{-15}}{\overset{k_{15}}{\rightleftharpoons}} H + H + M$	$k_{15} = 2.9\ 10^{-4} T^{-1.5} exp(-52007/T)$
		$\gamma_{-15} = 3\ 10^{-32}$

averaged conditions using RUNGE-KUTTA procedures. The most important incorporated species as well as the dominant electronic , ionic and thermal reaction channels are summarized in the table, using new reference datas [1] [4] [5].

Results and Discussion

In Fig. 2 the relative I_2 concentration is shown at different concentrations n_e of plasma electrons in the rf discharge at a constant gas temperature, starting from the same input composition. Independent of the averaged ionization degree an identical composition of the stable reaction products is formed, reflecting the CEEC. The same finite composition is produced at a vanishing ionization degree by the excitation of the mixture in a faint TESLA spark discharge (Fig. 2, open symbols).

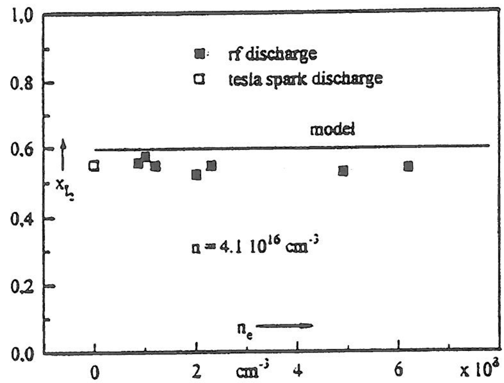

Fig. 2 Dependence of the relative I_2 concentration on the averaged concentration of plasma electrons (Reactor diameter: $9mm$, length: $120mm$, tube temperature: $360K$, rf frequency: $450kHz...610kHz$, input mixture: $x_{I_2 0} = 0.61$, $x_{H_2 0} = 0.39$, particle number density: $n = 4.1\ 10^{16} cm^3$)

The detailed analysis of the proposed reaction mechanism showed, that the extreme situation of the CEEC is estimated by a small number of elementary processes, which are emphasized in the table. The model calculations, using the tabulated rate coefficients, sufficently agree with the experimental results (Fig. 2, horizontal line). Within a factor two the CEEC is estimated by the following relation:

$$\frac{x^o_{H_2}\, x^o_{I2}}{x^{o\,2}_{HI}} \approx 0.5\, \frac{k_3\, k_{11}}{k_1\, k_{-10}}$$

Surprisingly the formula has the form of a Mass Action Law.

The combined thermal and plasma activation of the chemical conversion was studied at the admixture of a non-reactive He puffer gas. It enabled the relative fast

generation of the thermal equilibrium at higher temperatures ($\geq 350°C$), because the thermal reaction velocity depends quadratical on the total number density of the process gas. An example is given in Fig. 3, selecting the I_2 component: At a nearly constant spark discharge excitation ($P \leq 0.1W$) the temperature was changed within the range $20°C...500°C$. At lower temperatures the common excitation results in a nearly temperature independent CEEC. At higher temperatures the situation is controlled by the Mass Action Law.
An adequate model calculation is presented in Fig. 4 (index: model). For comparison the thermal product composition, estimated by the Mass Action Law MAL, is shown too (index: MAL). Corresponding with the above given explanation at low temperatures a electronically controlled composition is established, far from the thermal equlibrium (marked by CEEC, dominance of emphasized reaction channels). At higher temperatures the reactions (14) and (15) become more and more important, followed by the convergence of the MAL- and model- curves for highest T values.

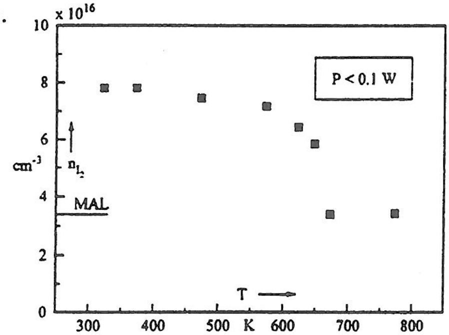

Fig. 3 Transition from the CEEC to the Thermal Equilibrium at common excitation by a TESLA spark discharge and thermal activation
(input concentrations: $I_2/\ H_2/\ He = 1.6\ 10^{17}\ /2.1\ 10^{17}\ /2\ 10^{19}\ cm^{-3}$)

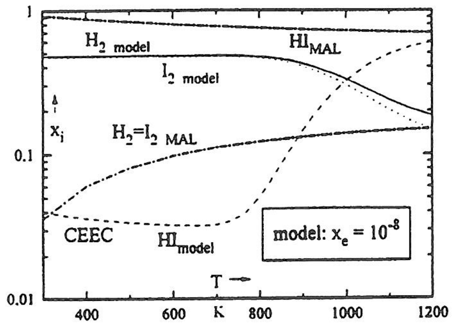

Fig. 4 Calculated composition of stable reaction products on the gas temperature for $x_e = 10^{-8}$, (input mixture: $x_{H_2} = x_{I_2} = 0.5$, $n_0 = 3\ 10^{17} cm^{-3}$)

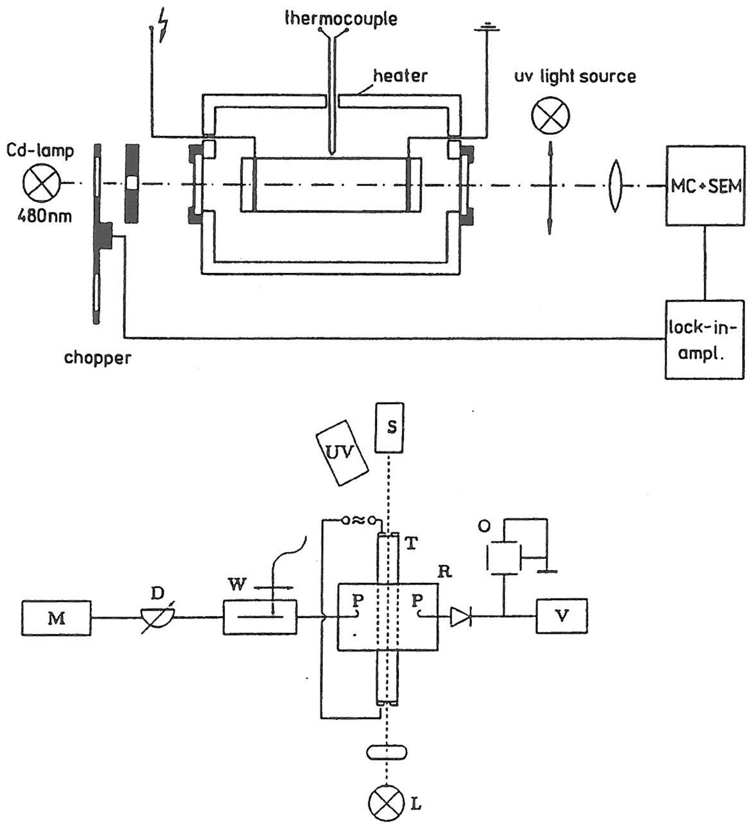

Fig. 1 Experimental setup

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