CHEMICAL KINETICS STUDY OF NITROGEN OXIDE SYNTHESIS IN A D.C. PLASMA JET : A PROPOSED MODEL

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INTRODUCTION. The experimental study of nitrogen oxide synthesis in a D.C. nitrogen-oxygen plasma jet shows that the final products, after quenching, have a concentration higher than the maximum predicted by equilibrium calculations at the same pressure /1/. Departure from equilibrium can be partially explained by chemical kinetics considerations :

quenching models from high temperature equilibrium have been proposed by POLAK /2/ from /3/ and /4/ and by AMMAN /5/.

I. COMPUTING METHOD. Let us consider a mixture of I chemical species A_i reacting in J chemical reactions with reaction rate constants k_j :

$$(I) \quad \sum_{i=1}^I \nu_{ji} A_i \xrightarrow{k_j} \sum_{i=1}^I \nu'_{ji} A_i$$

The thermodynamic temperature of the system is assigned to follow a law $T = f(t)$ which is supposed to describe the temperature history of the bulk gas from entrance of the torch to the end of the reactor. The pressure is assumed to be constant all along the system.

If diffusion processes are neglected the time dependence of the chemical composition of the system is calculated by solving the following differential system.

$$(2) \quad \frac{dy_i}{dt} = w_i - \left(\frac{y_i}{\rho} \sum_{j=1}^J w_j + \frac{y_i}{T} \frac{dT}{dt} \right)$$

where y_i is the molar concentration of the i^{th} species, $\rho = P/kT$ and w_i the production and loss terms for i^{th} specie.

$$(3) \quad w_i = \sum_{j=1}^J k_j (\nu'_{ji} - \nu_{ji}) \prod_{l=1}^I y_l^{\nu_{lj}}$$

if the initial concentration $y_i(0)$ are known, the differential system can be solved using the appropriate predictor-corrector method proposed by WINSLOW /6/.

II. REACTIONS AND REACTION RATE CONSTANTS. We have used data gathered by PRUD'HOMME /7/, and these recommended by BAULCH /8/.

At temperature below 5000 K only the following neutral species have been considered : N_2 , O_2 , NO, N and O. They are supposed to take part in the following reactions

The selected rate constants are listed in Table I. M is any one of the five species.

III. RESULTS. From some measurements performed on a nitrogen-oxygen plasma jet we have fitted the experimental time-temperature history along the reactor in the following manner. The temperature at each end of the reactor is 300K, the gas is heated up to 5000K in 10^{-5} sec. The initial value of the heating rate (dT/dt) is 10^9 K/s, its mean value is $5 \cdot 10^8$ K/s, the heating law is parabolic with time. A similar parabolic law is used for the quenching step during $9 \cdot 10^{-5}$ s with an initial rate - 10^8 K/sec.

Molar fractions versus time are shown in figure I. Figures II and III describe respectively the time evolution of the overall production of NO ($d(NO)/dt$) and N, and the production of NO and N by each of the reactions (4) to (9).

At the very beginning of the reaction ($t < 5 \mu\text{sec}$, $T < 4000$ K) the production of NO is due mainly to reaction (7), a result which is not in agreement with the conclusions of ZEL'DOVICH /3/ and POLAK /2/ for this process. At the same time N is produced by reaction (8).

The maximum production rate of NO is reached between 8 and 12 μsec ($T = 4000 + 5000 + 4800$ K) and processes (7) (8) and (9) produce an equivalent amount of NO. The production rate of N by process (8) is equal to the loss rate by process (9) and $[N]$ is maximum. Between 12 and 18 μsec ($T = 4800 + 4200$ K) the processes (7) (8) and (9) always produce NO but with a lower rate until a zero rate is reached at 18 μsec and the process (9) destroys N.

Between 18 and 60 μsec ($T = 4200\text{K} + 1500\text{K}$) reactions (8) and (9) slightly destroy NO. The destruction of N by the process (9) is higher than the production by (8).

From $t = 60 \mu\text{sec}$ ($T < 1500$ K) the system is partially frozen especially for NO since there is no more ato-

mic nitrogen and oxygen recombines very slowly by the process (4) which governs $[O]$ during the total reaction time.

Processes (5) and (6) are significant only at high temperature ($T > 4500$ K).

CONCLUSION. At 1 atm. the frozen high temperature equilibrium predicts a maximum of $[NO]$ of 7%, the kinetics model shows that it is possible to obtain up to 11 % (a result which is in good agreement with experiment /1/).

The important role of quenching rate is shown with our model, but, as far as we know, it is the only one which points out the equally important role of heating rate. The heating rate controls the maximum concentration of NO as the quenching controls the freezing of the high temperature mixture.

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	B	α	E	References
(4)d	$3.2 \cdot 10^{19}$	-1	118000	/III.28/à/III.34/
(4)r	$5 \cdot 10^{15}$	-2.5	0	/III.35/
(5)d	$4.1 \cdot 10^{22}$	-1.5	224900	/III.33/à/III.37/ /III.28/
(5)r	$1.2 \cdot 10^{17}$	-5	0	/III.36/ /III.38/
(6)d	$2.9 \cdot 10^{19}$	-1.	150000	/III.39/
(6)r	$4.3 \cdot 10^{20}$	-1.5	0	/III.40/
(7)d	$9.1 \cdot 10^{24}$	-2.5	128500	/III.34/
(7)r	$2.4 \cdot 10^{23}$	-2.5	85500	/III.41/
(8)d	$7 \cdot 10^{13}$	0	75500	/III.34/
(8)r	$1.3 \cdot 10^{11}$	0.5	0	/III.38/
(9)d	$1 \cdot 10^{11}$	0.5	6200	/III.42/
(9)r	$2.0 \cdot 10^{10}$	0.5	38400	/III.38/

Table I. Reaction rate constants. $k = B T^{\alpha} \exp(-E/RT)$

Figure I