STUDY OF THE NO SYNTHESIS IN A MICROWAVE PLASMA AT ATMOSPHERIC PRESSURE[1)]

P. TARAS[2)], V. DUŠEK[3)], J. VYSKOČIL[2)], Praha

This contribution shows that the microwave plasma ($f = 1.25$ GHz) generated in air at atmospheric pressure is basically in equilibrium, its temperature being only slightly dependent on the power absorbed (0.6—8 kW) and upon the air flow through the reactor (53—132 l/min).

ИЗУЧЕНИЕ СИНТЕЗА ОКИСИ АЗОТА В МИКРОВОЛНОВОЙ ПЛАЗМЕ ПРИ АТМОСФЕРНОМ ДАВЛЕНИИ

В работе показано, что микроволновая плазма ($f = 1,25$ ГГц), генерированная в воздухе при атмосферном давлении, находится в основном в состоянии равновесия. При этом ее температура только слабо зависит от поглощаемой энергии (0,6 – 8 кВт) и от потока воздуха, проходящего через реактор (58 – 132 л/мин.).

I. EXPERIMENTAL

The plasma used in this plasma chemical synthesis study was generated by absorbing microwaves of the frequency 1.25 GHz in air at atmospheric pressure, the power absorbed being up to 8 kW CW. The quartz discharge tube of 18 mm i.d. passed through the centre of the wider wall of the rectangular waveguide 228×40 mm. The parameters of microwave radiation transmitted by the waveguide line were computed from data obtained by the four-probe and calorimetric measurements. The product analysis was performed by means of the quadrupole mass spectrometer QMG 511 (Balzers), data evaluation and computing of the theoretical models was performed on a PDP-11 computer.

[1)] Contribution presented at the 5th Symposium on Flementary Processes and Chemical Reactions in Low Temperature Plasma. ŠTIAVNICKÉ BANE, May 21—25, 1984.

[2)] Institute of Plasma Physics, Czechosl. Acad. Sci., Po vodárenskou věží 4., 182 11 PRAHA 8, Czechoslovakia.

[3)] Institute of Physics, Czechosl. Acad. Sci., Na Slovance 2, 180 40 PRAHA 8, Czechoslovakia.

II. RESULTS AND DISCUSSION

The degree of non-equilibrium of a plasma which may be defined as the electronic (T_e) and gas (T_g) temperature difference, may be estimated theoretically [1]. Unfortunately, the derived value is valid only for the volume in which the microwave power is absorbed (roughly equal to the skin layer), which is very small compared to the whole volume of the plasma column. Moreover, the skin layer is very thin (for $T = 5000$ K less than 0.5 mm) and thus the assumption of neglect of diffusion apparently is not fulfilled. Thus, the temperature difference estimated with the aid of the formula found in literature [1] $T \doteq 2000$ K was not confirmed experimentally (neither by other authors [2] nor in this work).

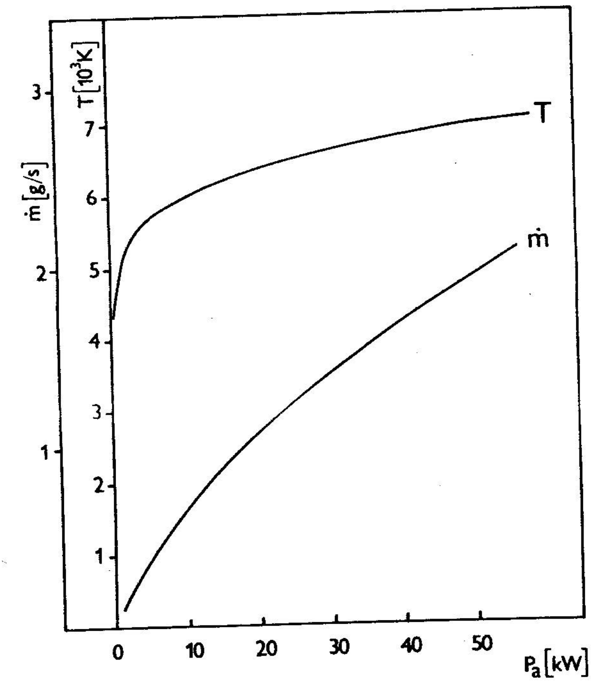

Fig. 1. Theoretical curves for plasma temperature (T) and gas-plasma throughput ($\dot{m}$) in dependence on power absorbed.

An experimentally derived fact that the product concentration is the parabolic function of molar fractions of both components,

$$c_{NO} = k_c c_{N_2}^a c_{O_2}^b, \qquad (1)$$

shows for the exponent values of $a \in (0.64 \pm 0.01)$ and $b \in (0.6 \pm 0.1)$ that the principal steps of the synthesis are in equilibrium [3]. A slight deviation of both exponents from the theoretical value of 0.5 may apparently be caused by the prompt, basically non-equilibrium, product quenching.

As it has been stated, the plasma is near the thermodynamic equilibrium and all its parameters may be assumed to be the functions of its temperature T.

A theoretical value of plasma temperature may be derived from incident power, plasma dimensions, type and flow of gas, using the analogy between the microwave discharge and the slow-burning process [4].

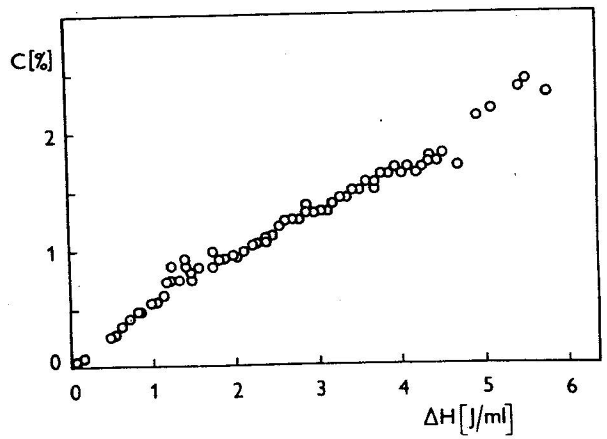

Fig. 2. NO concentration as the function of gas mean enthalpy for various experimental conditions.

Solving a simple stationary problem with the assumption that the skin depth is much smaller than the plasma dimensions, we get the relation for plasma temperature and the absorbed microwave power. The temperature vs. power dependence for a tube of 18 mm i.d. is presented in Fig. 1. It can be seen that plasma temperature is only slightly affected by the power alterations.

The plasma temperature derived in this way agrees with that from a dynamic model (which takes into account gas flow as well) with an accuracy of the order of T/I (approx. 0.03), where I is the ionizing potential of air [4].

In a series of experimentally observed relations between NO concentrations and the absorbed power (at constant flows) nearly linear of the type

$$C_{NO} = k_f P_a \tag{2}$$

were found, whilst the slopes k_f were indirectly proportional to the corresponding values of gas flows through the reactor

$$k_f = K/F, \tag{3}$$

where F denotes the gas flow, K is a constant.

By combining the Eqs. (2) and (3) we get

$$\frac{C_{NO}}{P_a} = K. \tag{4}$$

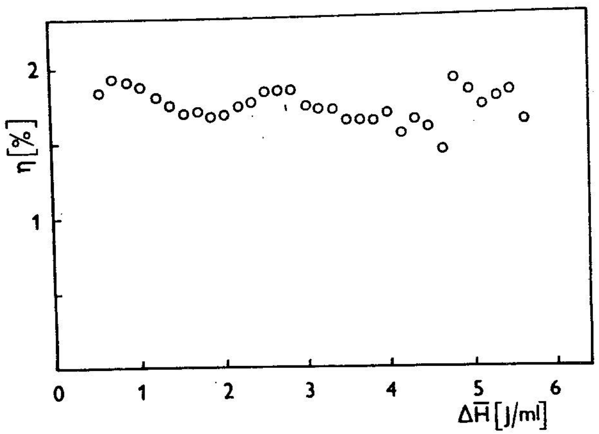

Fig. 3. Experimentally obtained efficiencies for different mean enthalpies.

This relation demonstrates that the concentration of the produced nitrogen oxides depends in the first approximation upon the ratio P_a/F (mean gas enthalpy) only. This is illustrated by Fig. 2.

By comparison of Eq. (4) with the definition of the energetic efficiency of the synthesis

$$\eta = const. \frac{C_{NO} F}{P_a} \tag{5}$$

we can see that, when accepting the aforementioned approximations, we can take the efficiency of the synthesis within the studied conditions as constant.

Deviations from the average value of $\bar{\eta} = 1.75$ % are apparently a function of $\Delta\bar{H} = P_a/F$ (see Fig. 3) and may be caused by resonance effects in the discharge zone. It is to be noted here that $\Delta\bar{H}$ is the mean value for the whole reaction zone, including both the plasma column and the surrounding cold gas.

If we compare the mentioned statement with the theoretical efficiency vs. gas enthalpy dependence (see Fig. 4) based on data from literature [5], we can judge that the temperature of the plasma under study did not alter when changing both the absorbed power and/or the total gas flow. Thus, the most markedly affected parameter by the absorbed power changes is the amount of gas passing through the plasma region $\dot{m}$.

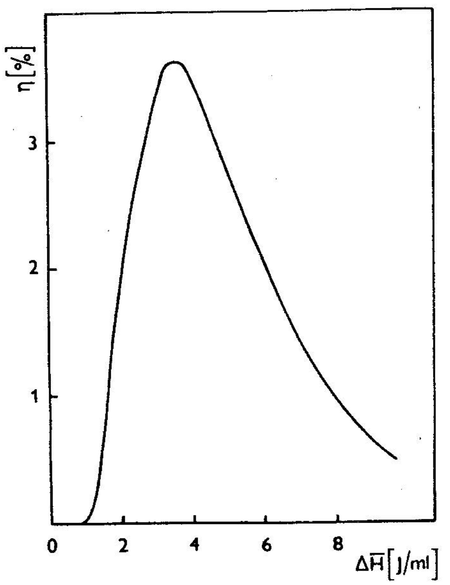

Fig. 4. A theoretical dependence of the equilibrium synthesis efficiency upon air enthalpy at atmospheric pressure.

Taking into account the supposition of plasma symmetry, neglect of diffusion, radiation and energy loss on the discharge tube wall in addition to foregoing assumptions, the theoretical dependence of the $\dot{m}$ value upon the absorbed power was derived. This dependence (nearly linear) is given in Fig. 1. The value of $\dot{m}$, under these suppositions, does not depend on the total gas flow F.

The facts found during this study indicate a possibility of generating plasma with constant temperature. From the point of view of the NO synthesis, however, this temperature is too high (5000—5500 K). The maximum efficiency in an equilibrium system is achieved at a temperature of some 3000 K, which corresponds to an enthalpy increase of approx. 3.6 J/ml (see Fig. 4).

III. CONCLUSIONS

The experimental results show that the microwave plasma under study was in fact in equilibrium. The dependence of the product concentration upon the mean gas enthalpy indicates that the efficiency keeps constant, which is apparently a consequence of the invariability of plasma temperature.

The theoretical analysis of the problem fully confirms and explains the experimentally observed facts.

REFERENCES

[1] Ginzburg, V. L.: *Rasprostranenie elektromagnitnych voln v plazme.* Nauka, Moskva 1967.
[2] Arata, Y. et al.: Transaction of JWRI 3 (1974), 11.
[3] Taras, P. et al.: Acta Phys. Slov. 33 (1983), 175.
[4] Rajzer, J. P.: *Lazernaya iskra i rasprostranenie razryadov.* Nauka, Moskva 1974.
[5] Predvoditelev, A. S.: *Tablicy termodinamicheskikh funkcií vozdukha.* Nauka, Moskva 1962.

Received June 8th, 1984
Revised version received September 27th, 1984