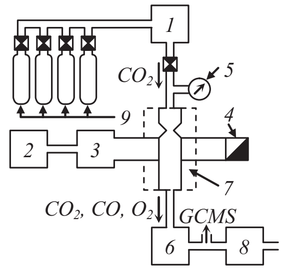

Figure 5–45. Schematic of an experiment with supersonic plasma-chemical microwave discharge: (1) CO_2 gas inlet system; (2) power supply; (3) microwave generator; (4) tuning system; (5) manometer; (6) heat exchanger; (7) microwave plasma reactor; (8) vacuum pump; (9) CO_2 gas tanks.

of CO_2 dissociation in non-equilibrium plasma (maximum power of the discharge is about 1 MW; Asisov et al., 1981a,b, 1983). A schematic of the experiments is shown in Fig. 5–45. The plasma-chemical reactor is arranged in a quartz tube (after a supersonic nozzle) with a diameter of 3.5 cm and effective length of 30 cm, crossing a waveguide. The critical cross-sectional diameter of the supersonic nozzle is 0.8 cm, and the expansion degree is about 20. The initial pressure in the tank before the nozzle varies from 1.8 to 7 atm, which corresponds to static pressure in the plasma-chemical reactor from 0.05 atm (40 Torr) to 0.2 atm (150 Torr) and to flow rates of 5–50 L/s. This pressure range is optimal for process stimulation by vibrational excitation. Distributions of static pressure along the axis of the nozzle and the microwave discharge chamber with and without discharge are shown in Fig. 5–46. These distributions as well as the values of flow rate measurements prove that the flow remains supersonic in the presence of microwave plasma. The experimental Mach number value is in the range $M \approx 2$–3, in good agreement with calculations based on the nozzle geometry. The electron density, measured in the discharge chamber by means of microwave interferometry on wavelength $\lambda = 0.3$–0.8 cm, varies in the range $3–8 \cdot 10^{12} cm^{-3}$; the electron temperature is about 1 eV. The vibrational temperature was determined in these experiments by measurements of the Doppler broadening of spectral lines of alkaline atoms, which were in quasi equilibrium with vibrational degrees of freedom of CO_2 molecules (Givotov et al., 1985b). The vibrational temperature in the optimal regime was found to be $T_v \approx 3500\,K$, while the translational gas temperature, $T_0 \approx 160\,K$ (!), remained below room temperature. Gas composition was measured by chromatography and by gas analyzers. The energy efficiency of CO_2 dissociation corresponding to these measurements is shown in Fig. 5–44. The minimum energy cost of the CO_2 dissociation process, measured in these experiments, was 3.2 eV/mol, which corresponds to the record high energy efficiency of 90%.

5.6.5. Gasdynamic Stimulation of CO_2 Dissociation in Supersonic Flow: "Plasma Chemistry Without Electricity"

Stimulation of CO_2 dissociation can be achieved not only by means of an increase of gas temperature (better the vibrational one) but also by means of cooling the gas(!). It

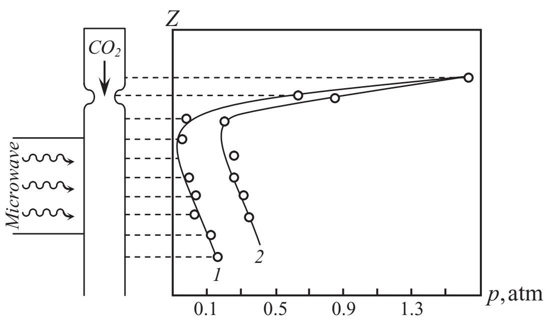

Figure 5–46. Evolution of static gas pressure along axis of supersonic plasma-chemical system: (1) without discharge; (2) in presence of microwave discharge.

sounds non-realistic at first, but it is correct theoretically and proven experimentally. The explanation is simple: the dissociation rate in non-equilibrium systems depends not only on vibrational temperature (T_v) of CO_2 molecules but also strongly on the degree of VT non-equilibrium (T_v/T_0) (see, in particular, Section 5.2.5 and relation (5–26)). If the level of VT non-equilibrium (T_v/T_0) is high, the Treanor effect leads to a significant overpopulation of highly vibrationally excited states even at relatively low values of vibrational temperature. In other words, gas cooling can accelerate the endothermic process almost as effectively as heating. A significant decrease of translational gas temperature T_0 ("gas cooling") without essential reduction of vibrational temperature T_v of CO_2 molecules (and as a result, strong VT non-equilibrium $T_v \gg T_0$, strong Treanor effect, and effective CO_2 dissociation) can be done in a supersonic nozzle, similarly to the case of supersonic plasma considered in Sections 5.6.1–5.6.4. Most of the energy accumulated in CO_2 vibrational degrees of freedom before a supersonic nozzle can be localized through the Treanor effect in highly excited levels after the nozzle and, finally, transferred into CO_2 dissociation.

This interesting effect of **gasdynamic stimulation of CO_2 dissociation in supersonic flow** is similar to plasma-chemical CO_2 dissociation but doesn't require direct consumption of electricity to sustain the plasma. For this reason the effect sometimes is referred to as "**plasma chemistry without electricity**." The effect of gasdynamic stimulation of dissociation is somewhat similar to gasdynamic lasers (Losev, 1977), but non-equilibrium vibrational energy is transferred in this case into a chemical reaction instead of radiation. The phase "plasma chemistry without electricity" is due to first experimental observation of the effect. The electricity used to sustain microwave plasma was turned off in a supersonic plasma-chemical experiment, but dissociation of CO_2 in the supersonic flow remained at a significant level even though the initial gas temperature was 300 K(!). The effect can be observed not only in CO_2 dissociation but also in other endothermic processes stimulated by vibrational excitation (Rusanov et al., 1982; Zhdanok & Soloukhin, 1982; Asisov et al., 1986). One can say that the gasdynamic stimulation effectively increases the "kinetic temperature" of the gas. It means that, due to the Treanor effect even at room temperature, the CO_2 dissociation rate is equivalent to that at more than 2000 K in quasi equilibrium. The conversion degree, however, corresponds to the total energy accumulated in vibrational degrees of freedom at actual CO_2 temperature. Obviously, the gasdynamic stimulation effect is not limited to CO_2 dissociation and can be applied to other gases where the Treanor effect is strong enough, for example CO, N_2, and H_2. Experimental results on the gasdynamic stimulation of CO_2 dissociation in supersonic flow with Mach number $M \approx 6$ (Asisov et al., 1986) are shown in Fig. 5–47 in comparison with kinetic simulations at Mach numbers ($M = 4.5, 5.5, 6.5, 9.5$) corresponding to $T_v/T_0 = 5, 7, 10, 20$. The figure presents CO_2 conversion degree α as a function of initial gas temperature before the supersonic nozzle. As one can see, the conversion degree can reach the level of 1–3% without direct use of electricity and without significant heating of the gas. At room temperature (that is without heating at all!), the CO_2 conversion degree is not high (about 0.2%) but is quite visible.