Interaction of Atomic Hydrogen with Charcoal at 77 K

A.E. Gorodetsky 1), S.P. Vnukov 1), R.Kh. Zalavutdinov 1), A.P. Zakharov 1), A.K. Buryak 1), A.V. Ulyanov 1), G. Federici 2), Chr. Day 3)

1) Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, Russian Federation
2) ITER Garching Joint Work Site, Garching, Germany
3) Institut für Technische Physik, Forschungszentrum Karlsruhe, Germany

e-mail contact of main author: gorodetsky@ipc.rssi.ru

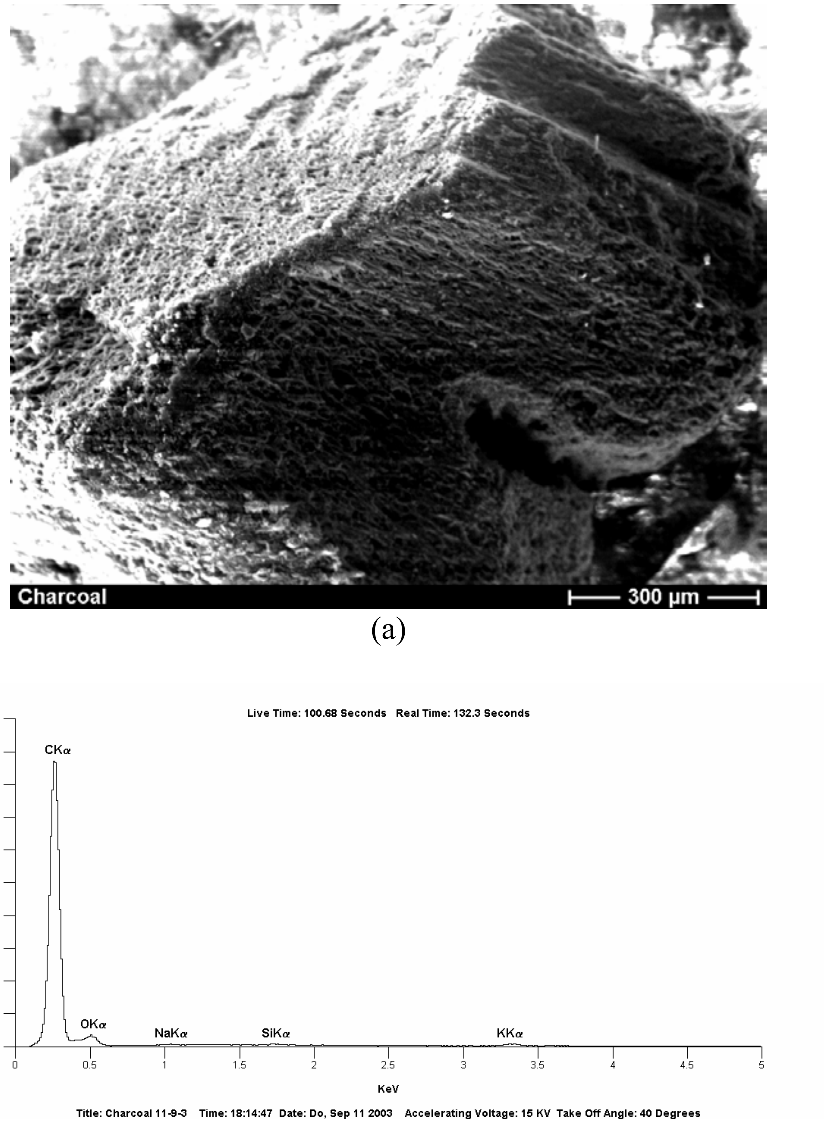
Abstract. Charcoal is a working material of sorption cryopumps in the ITER project. The interaction of thermal hydrogen molecules and atoms with charcoal has been analyzed by TDS (77-300 K) and sorption measurements at 77 K. A stream quartz reactor with an H_2 RF discharge was used for the production of H atoms. The ratio of H and H_2 in the gas mixture in the afterglow zone was ~10^{-4}, hydrogen flow and inlet pressure were 6.9 sccm and 30 Pa, respectively. After exposure in the H/H_2 mixture during 1 hour the marked change in the shape of the TD spectra and decrease of the charcoal sorption capacity for hydrogen and nitrogen were detected. A wide spectrum of hydrocarbon fragments formed at 77 K was registered by mass-spectrometry at charcoal heating up to 700 K. The specific adsorption volume of charcoal, which was measured by N_2 adsorption at 77 K, decreased directly as amount of H atoms passed through the section with charcoal.

1. Introduction

When the inner surface of the ITER pumping duct is covered with a thin a-C:H film, the hydrogen recombination coefficient in the reaction H(gas)+H(surf.) can be significantly reduced and reach a value of 10^{-3}. In this case the atomic hydrogen can arrive at the cryopump region [1] and interacts with charcoal (cryosorbent of vacuum pump [2, 3]). In the present work the interaction of thermal hydrogen molecules and atoms with charcoal has been analyzed by sorption measurements at 77 K and thermodesorption (TD) experiments at 77-300 K.

2. Some Physicochemical Characteristics of Charcoal

The candidate charcoal type for the ITER cryosorption vacuum pumps is a microporous sorbent produced by industry in the form of granules with size of ~1 mm *(FIG. 1a)* and has a poured density of 0.45-0.48 g/cm^3. Densities of charcoal at dipping into mercury and exposure in helium are 0.8 and 2.0 g/cm^3, respectively [3, 4]. The sorbent contains the small amounts of impurities such as oxygen and alkaline metals *(FIG. 1b)*. The average micropore size usually is close to 1 nm and total pore volume is ~1 cm^3/g. Charcoal specific surface may run to 1500 m^2/g [3, 4]. The sorbents are produced from carbon-containing raw materials (coconut shell) by carbonization at ~1300 K with successive activation in water vapour 1000 K. In literature such sorbent is called as “charcoal” [3, 4]. The charcoal granules are sufficiently hard and rigid. The granules are formed from crystallites containing the graphite-like nets with sizes 1-3 nm. The crystallites are connected with the layers of amorphous carbon. The ITER charcoal sorption capacity measured by molecular hydrogen reaches a huge value of 100-200 and 600-700 cm^3 (SPT)/g at 77 and 16 K, respectively, [3, 4]. H/C ratio in charcoal is equal to 0.2-1.0 and hydrogen density inside the sorbent is comparable with density of solid hydrogen (0.076 g/cm^3).



(a)

(b)

FIG. 1. Micrograph of a charcoal granule in secondary electrons (a) and composition of charcoal (b). There are impurities of Na, Si and K in the sorbent. Oxygen peak is connected with water adsorption on charcoal.

3. Experimental

In the experiments with charcoal we used the so-called "stream technique" [5]. In this technique an analysed sample is exposed in a laminar gas flow with controlled parameters. The stream technique allows providing the exposure of the charcoal in the flows of any gases and gas mixtures and in particular to expose the charcoal in the flows of atomic hydrogen or hydrocarbon radicals in the temperature range 77-1000 K. In the frame of the stream technique is it possible to obtain the thermodesorption spectra during heating of the charcoal samples from 77 up to 300 K in the flow of an investigated gas or gas-carrier.

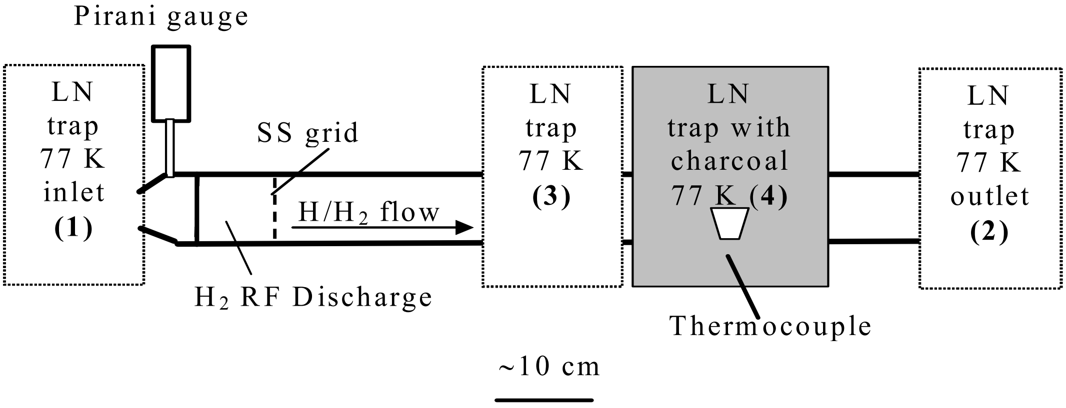


FIG. 2. Scheme of the quartz gas flow reactor with 1 cm radius and 100 cm length for experiments with charcoal in atomic/molecular mixture at 77 K. Gas flow controllers were installed at the tube inlet.

A cylindrical quartz reactor of 100 cm length and 1 cm radius was the main part of the setup. The pressure difference between inlet and outlet of the tube did not exceed 2 Pa. In the majority of the experiments the laminar flow velocity, **V**, was equal to 110-120 cm/s (Re≈2, Knudsen number Kn≈0.01). A residence time of gas particles in the tube averaged out to ~0.5 s. The reactor was pumped out by a rotary pump. An H_2 RF inductive-coupled discharge (frequency 20 MHz, specific power 0.1 W/cm^3) in a flow of 6.9 sccm (3.1×10^{18} H_2/s) under a pressure of about 30 Pa has been utilized for production of atomic hydrogen. A plasma region of about 15 cm length was limited by a thin (100 μm) stainless steel grid. Hydrogen was used with a purity of 99.9999 vol.%.

For determination of the flows and atomic hydrogen concentration at the various tube regions we used solid carbon films (H/C=0.4) which were deposited on silicon substrates in the Institute of Plasmaphysics in Garching, Germany. An erosion coefficient of solid carbon films at 650 K in the medium of atomic hydrogen is well known (Y=0.02) [6]. Measuring film areal densities (by means of Electron Probe Microanalysis) before and after exposure in atomic hydrogen environment it is possible to determine the erosion rate and, thus, the H atom thermal flow (~10^{16} H/cm^2 s) and concentration (~10^{11} H/cm^3, T=650 K) at a certain tube place.

A semiquantitative assessment of an atomic and molecular hydrogen ratio in a mixture in the region of a copper container with charcoal gave a value $H/H_2 \approx 10^{-4}$ at laminar molecular hydrogen flow rate of 6.9 sccm. This H/H_2 composition is considered to be characteristic for all the measurements described in this paper.

We have used three LN traps for deep purification of inlet gas from impurities. Two traps (1 and 2) were placed on the tube inlet and outlet. The third trap was located directly before the container with charcoal *(see FIG. 2)*. In this trap the water vapours formed as a result of atomic hydrogen interaction with the quartz were condensed.

The container with charcoal was cooled by the forth LN trap. The charcoal mass was 6-60 mg. In the experiments we used the samples taken from the package (not reclaimed) or regenerated in vacuum (background pressure 4 Pa) at 620 K. A thermocouple was placed under the container with charcoal at an external tube side. In the control experiments the thermocouple was placed directly under the container with charcoal inside the tube.

In reference experiments the non-reclaimed sample (weight 21 mg) of charcoal was exposed during half an hour (T=77 K) in nitrogen, methane, molecular hydrogen, argon flows (6.9 sccm), and residual gas (T=140 K), in which mass-spectra the masses of 28, 32, and 44 were predominant. After exposure the tube section No 4 with charcoal *(FIG. 2)* was heated up to room temperature at continuous measurements of the pressure in the tube by Pirani gauge (TR 901, LH Leybold Inficon Inc., Germany) and temperature of the tube wall by the thermocouple. In this case the three remaining traps were at LN temperature. The inlet flow rate of the investigated gas remained invariable as the temperature increased. The heating rates were 10 and 4-5 K/min in the temperature ranges 77-250 and 250-300 K, respectively. TD peak characteristics of adsorbed gases are indicated in Table I. The thermodesorption (TD) spectra of these gases are shown in *FIG. 3* (pressures are given in Pirani readings).

To determine the gas amount in the TD peak its area was measured in pressure increment – time coordinates. A proportionality coefficient between this area and the amount of released gas was found in special calibrating experiments.

TABLE I: TD PEAK CHARACTERISTICS IN REFERENCE EXPERIMENTS.

Gas	The test conditions: pressure (Pa), temperature (K)	Amplitude (Pa) and temperature (K) of the TD peak	FWHM, ΔT (K)	Sorption capacity (cm^3/g)
Nitrogen, N_2	44, 77	1.7, 145	50	40
Methane, CH_4	34, 77	2.8, 155	60	100
Hydrogen, H_2	32, 77	0.6, 130	50	10
Argon, Ar	48, 77	0.5, 140	50	~6
Residual gas	4.26, 140	1.87, 250	10	~6

Note: FWHM – the full width at half maximum of a peak

Before the experiments with the H_2/H RF discharge the sample of charcoal (weight 24 mg) was regenerated in vacuum (pressure 4 Pa, maximum temperature 620 K) in the tube.

The regenerated in-situ sample was exposed in molecular hydrogen (77 K, 32 Pa, 30 min). The tube section No 4 *(FIG. 2)* with charcoal was heated up to room temperature at the continuous measurement of pressure in the tube by the Pirani gauge and temperature of tube wall by the thermocouple. In this case the inlet H_2 flow rate was constant and the three remaining traps were at LN temperature. Thus, we obtained the first hydrogen TD curve *(FIG. 4)*. Then the sample was exposed in the afterglow zone of the H_2/H RF discharge (77 K, 32 Pa, 180 min). After charcoal exposure in the H/H_2 mixture the RF discharge was switched off and the second TD spectrum was obtained in the same way as in the reference experiments. Finally, for the third time the sample was cooled down to 77 K and then was exposed to molecular hydrogen again (77 K, 32 Pa, 30 min). The last third spectrum evidenced the change of active carbon sorption properties resulting from exposure to the H/H_2 mixture. The similar set of experiments in the tube (in-situ) was carried out with methane in use as an exploring gas *(FIG. 4, curves 4 and 5)*. The total amount of released gas in the CH_4 TD peak

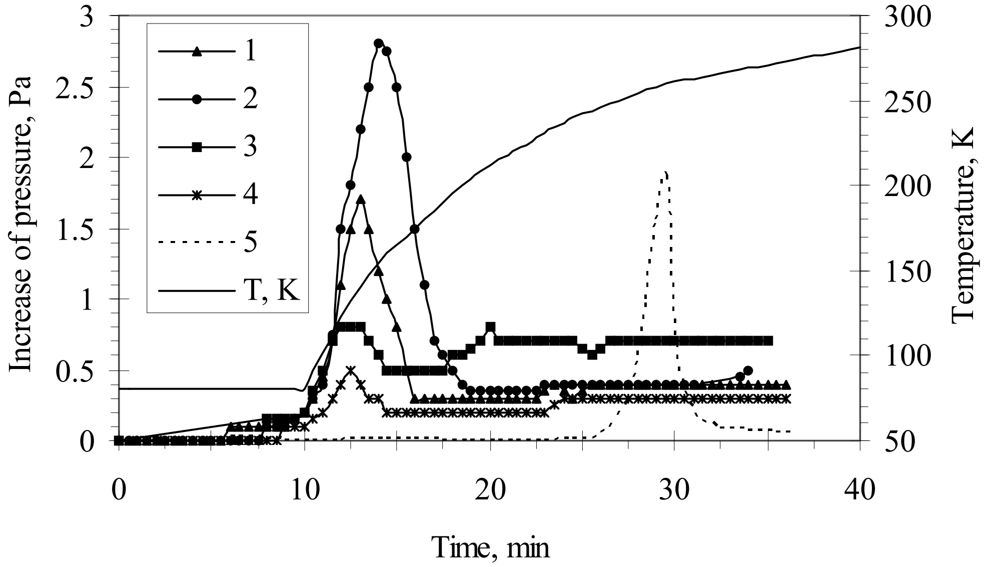


FIG. 3. Nitrogen (1), methane (2), hydrogen (3), argon (4), and residual gas (5) TD spectra for charcoal. Exposure conditions see in Table I.

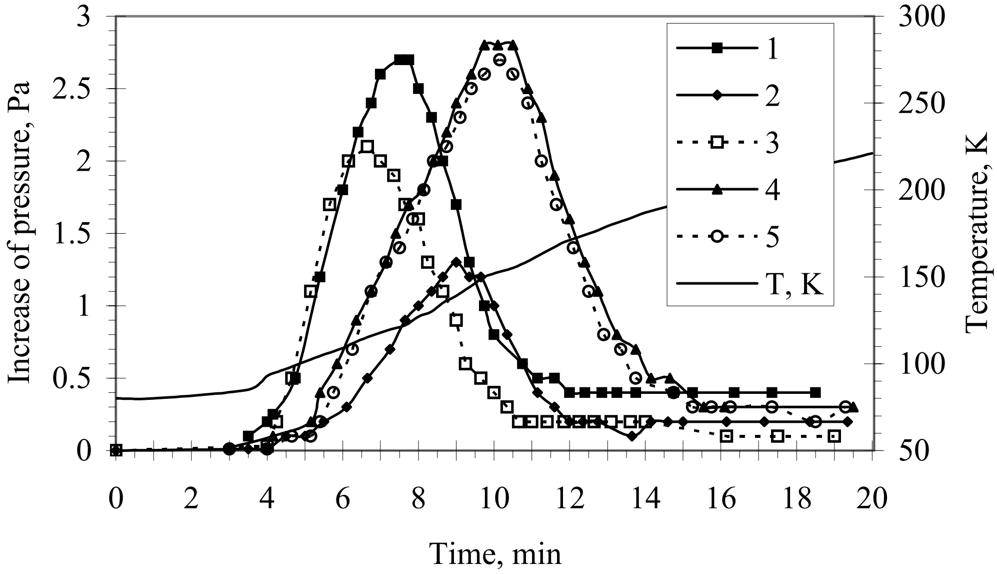


FIG. 4. Hydrogen (1-3) and methane (4, 5) TD spectra for charcoal (77 K, 32 Pa). 1 – after exposure in molecular hydrogen (30 min); 2 - after exposure in H/H_2≈10^{-4} mixture (180 min); 3 - after exposure in molecular hydrogen (30 min), obtaining the first TD spectrum, exposure in the mixture (60 min), obtaining the second TD spectrum, exposure in molecular hydrogen (30 min); 4, 5 – before and after exposure in the mixture (30 min).

(FIG. 4, curve 4) is nearly twice as large as that for the H_2 TD peak *(FIG. 4, curve 1)* because of differences in pumping rates of methane and hydrogen. The reasons of differences in ratio of hydrogen and methane amounts in *FIGS. 3* and *4* are not yet clear.

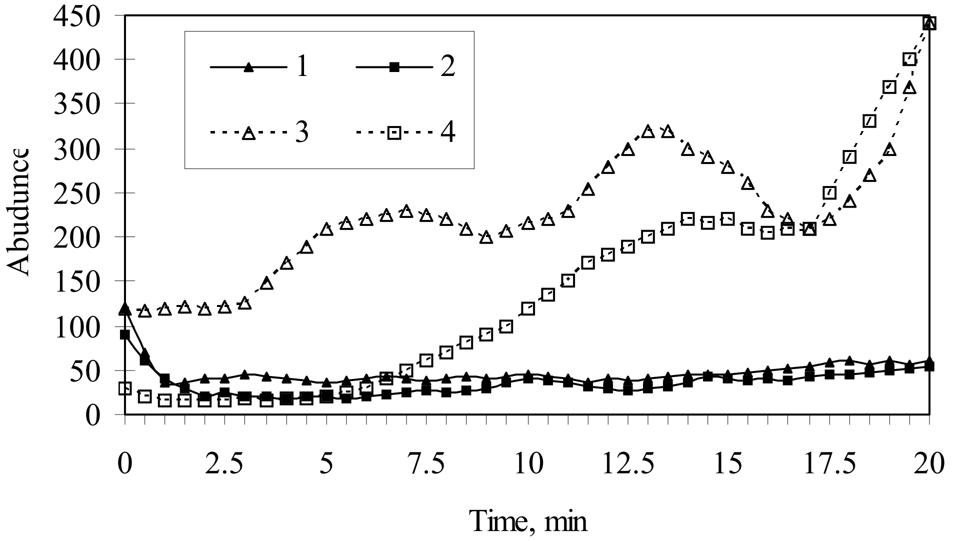


FIG. 5. Temperature programmed desorption spectra for charcoal before (1, 2) and after (3, 4) the $H/H_2 \approx 10^{-4}$ mixture exposure (77 K, 34 Pa, 1 hour, 55 mg charcoal). Heating rate is 20 K/min in the temperature range 300-700 K. 1, 3 – m/e=43; 2, 4 – m/e=55.

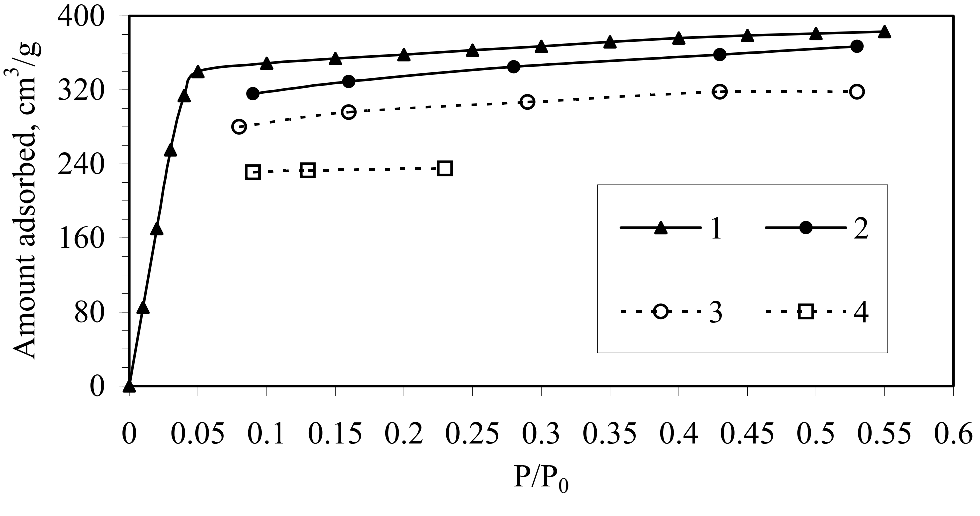


FIG. 6. Nitrogen adsorption isotherms for charcoal before (1, 2) and after (3, 4) exposure in the H/H_2 mixture. 1 – [4]; 2 – our experiment (77 K, 30 Pa, 6.9 sccm); 3 and 4 – after 2 and 4 hours exposure.

In a special experiment immediately after the exposure in the H/H_2 mixture and transfer through air the charcoal sample was analyzed in a mass-spectrometer with linear sample heating (20 K/min) up to 700 K directly in the equipment *(FIG. 5)*. In the temperature range

300-700 K the hydrocarbon ions were found with masses of 41 (C_3H_5), 43 (C_3H_7), 55 (C_4H_7), 57 (C_4H_9), and others. These hydrocarbon species were not observed at all in a mass-spectrum of the initial charcoal. In this analysis the absolute quantities of hydrocarbons formed were not determined. However, a wide spectrum of the appeared heavy hydrocarbons pointed to the intensive chemical interaction of atomic hydrogen with charcoal surface at 77 K as well as in [7].

Specific adsorption volume (SAV) of charcoal was measured ex-situ before and after the samples (weight 7 mg) exposure in the H/H_2 mixture *(FIG. 6)* with using a compensative volumetric technique. The compensative volumetric technique of SAV measurement is based on the determination of adsorbed nitrogen quantity at 77 K in the nitrogen pressure range $(0.01\text{-}0.5)\times P/P_0$. In the experiments the total amount of H atoms passed through the tube section with charcoal was about 1 cm^3 (for 4 hours). Decreasing of sorption volume (N_2) made up about the same magnitude.

4. Results and Discussion

From the adsorption-desorption experiments it is evident that irreversible hydrogen sorption takes place at charcoal exposure in the H/H_2 gas mixture. Registration of a wide spectrum of heavy hydrocarbon products after the H/H_2 exposure correlates with this finding.

We want to note the following peculiarities of H_2 TD spectra.

1) The total amounts of gas species (0.2-0.3) cm^3 adsorbed at exposure in the H/H_2 mixture are 2.5 times less than hydrogen quantity stored up at the first exposure in the molecular hydrogen (0.5-0.8) cm^3. In the second TD curve the low-temperature part of the initial spectrum changed essentially. This may be explained by the heat release at hydrogen atoms sorption. This may be explained by the heat release at hydrogen atom sorption.

2) At the third exposure of the sample in molecular hydrogen the stored hydrogen was 30% less than in the first experiment. In the third TD curve the high-temperature part of the initial spectrum changed as well.

It can be supposed that the indicated peculiarities of the first, second, and third TD curves are connected with a special bottle-like shape of the micropores in the charcoal [8]. Reactions between H atoms and surface C atoms with formation of hydrocarbon fragments take place in the micropores inlet.

When we used the methane as an exploring gas adsorbate a difference in the forth and fifth TD curves was less significant. However, a tendency to decrease the sorbed gas amount in charcoal exposed in the H/H_2 mixture preserved. The experiments carried out showed that the quantity of disappeared centres for hydrogen adsorption is comparable with the quantity of H atoms passed through the tube section with the samples. The performed assessments of the numbers of H atoms and adsorption centres allow supposing that in the experiment conditions the charcoal is an infinite sink for H atoms.

5. Conclusions

Irreversible hydrogen sorption takes place at charcoal exposure in the H/H_2 gas mixture at 77 K. Molecular hydrogen TD spectra of charcoal (77-300 K) undergo significant changes after the contact with the H/H_2 mixture. Different heavy hydrocarbon fragments appear in the reaction products at interaction of atomic hydrogen with charcoal at 77 K, which indicates chemical reactions. Specific adsorption volume (N_2 adsorption at 77 K) of charcoal decreases after reactions with atomic hydrogen. After H atoms interaction with charcoal the number of adsorption centres for molecular hydrogen and nitrogen decreases directly with the amount of H atoms passed through the tube section with charcoal. However, this effects may not be of ultimate importance to the cryosorbent application in ITER, which is characterized by the low pressure branch *(FIG. 6, curve 1)* rather than by the asymptotic limit for $P/P_0>0.1$. Furthermore, the ITER pumping concept does not rely on high saturation capacities of pumped gas amounts, but is defined by significant inventory limitation due to explosion safety hazards. Further tests are ongoing.

Acknowledgements

This research was supported by Forschungszentrum Karlsruhe, Germany under Contract 320/20283971/ITP.

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