EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH CERN - MT DIVISION

CERN-MT/95-10 (SM)

PUMPING CHARACTERISTICS OF THE St707 NON-EVAPORABLE GETTER (Zr 70-V 24.6-Fe 5.4 wt%)

C.Benvenuti and P.Chiggiato
CERN, 1211 Geneva 23, Switzerland

ABSTRACT

The room temperature pumping speeds of the St707 Non-Evaporable Getter (NEG) have been measured both for individual gases and for gas mixtures as a function of the quantities of gas pumped. The interesting feature of this NEG consists in its moderately low activation temperature. Therefore particular attention has been devoted to defining the optimum temperature and duration of the activation process to obtain the highest possible pumping speed in a given practical situation. It has been found that heating at 400° C for about one hour, or at 350° C for one day, results in pumping speeds of about 1000 $ls^{-1}m^{-1}$ for H_2 , 2000 $ls^{-1}m^{-1}$ for CO and 450 $ls^{-1}m^{-1}$ for N_2, values very close to those obtained after activation at the higher temperature of 740° C. The St707 NEG is therefore particularly suitable for passive activation during bakeout of stainless steel vacuum systems, avoiding the need of electrical insulation and feedthroughs which are mandatory when activation is carried out by resistive heating.

Geneva, October 1995

1. INTRODUCTION

Non-Evaporable Getters, in the form of a coated strip, may provide an ideal linear pump for conductance limited vacuum systems such as those of particle accelerators [1,2].
In recent years the Large Electron Positron collider (LEP), built at CERN, has been equipped with linear NEG pumps which provide about 95% of the total installed pumping speed over a length of about 23 km [3,4].
The NEG used for LEP is produced by SAES Getters under the trademark of St101 and consists of a Zr84-Al16 (wt%) powder cold sintered on a constantan ribbon [5]. It requires heating at 740° C for about 45 minutes for activation, which in the case of LEP is obtained by resistive heating (circulating current about 95A). The pumping characteristics of the St101 NEG have been extensively studied and the results are published elsewhere [6,7].
In spite of the successful application to LEP, the high activation temperature of the St101 NEG may be an insurmountable obstacle in other cases for mechanical reasons, particularly when considering the present trend towards particle accelerator vacuum chambers of smaller size and complicated geometry [8]. To overcome this inconvenience SAES Getters has developed and commercialised another NEG, under the trademark of St707 (Zr70-V24.6-Fe 5.4 wt%), which may be activated at lower temperatures, i.e. below 450° C [9].
The low activation temperature of the St707 NEG allows its activation during the bakeout of the (stainless steel) vacuum system. This passive mode of activation eliminates the need for power supplies, electrical feedthroughs and insulation. Consequently large amounts of NEG may be inserted in small volumes, resulting in larger pumping speed and lower ultimate pressure [2,10]. With this solution, a pressure in the low 10^{-14} Torr range has been achieved inside a 3 m long vacuum chamber [11,12].
In the present paper results are reported on pumping speed measurements of the St707 NEG for CO, N_2, H_2 and mixtures of these gases. Preliminary results on this subject are published elsewhere [10]

2. MEASURING APPARATUS AND PROCEDURE

All measurements reported in this paper have been carried out on NEG strips 30 mm wide.
Pumping speed measurements have been performed on short samples (25 cm long) activated inside a Fischer-Mommsen measuring dome [13] pumped by a turbomolecular pumping station and equipped with a residual gas analyser. The sample may be resistively heated to any desired temperature, which is measured with a thermocouple and an optical pyrometer.

Prior to NEG activation the measuring vacuum system is baked at 150° C when the activation temperature is 400° C or lower, or at 300° C for higher activation temperatures. The ultimate pressures obtained after a 24 h bake are below $2x10^{-10}$ Torr.

Pumping speed measurements are carried out with the NEG at ambient temperature only. The gas injection rate is kept in the range between about 1×10^{-7} and 3×10^{-5} Torr ls^{-1}, and under no circumstances does the pressure exceed the 10^{-6} Torr range on the injection side of the measuring dome. To avoid accumulation of the gases which are not pumped by the NEG (such as CH_4 and rare gases) a reduced turbomolecular pumping speed (2.3 l/s) is supplied during all measurement cycles. In order to avoid errors caused by residual gas adsorption, before each measurement the NEG is heated to 250° C for about 10 minutes.

Pressure measurements are carried out by means of two Bayard-Alpert ionisation gauges which have been previously calibrated for absolute sensitivity with about 15% uncertainty [14] and recalibrated in situ relatively to each other by downstream gas injection. The latter operation cancels measuring errors on injection rates and total injected gas quantity.

However, the uncertainty on the measured pumping speed values is affected by the uncertainty on absolute gauge calibration, which is about 15% as mentioned above, and increases to about 20% close to NEG saturation because of the uncertainty on the effective pumping speed value of the turbomolecular pump.

3. EXPERIMENTAL RESULTS

The pumping speed values of St707 measured as a function of the quantity of gas pumped and after 45 minutes activation at 300° C, 400° C, 500° C, 600° C, are reported in figs. 1 and 2. In order to provide an easier comparison with the performance of St101, the pumping speed curves of the two NEGs measured after the standard activation cycle for St101, that is heating at 740° C for 45 minutes [6,7], are shown together in fig. 3.

As already observed for the St101 NEG, the pumping speed curves for CO and N_2 present a large decrease consequent to increasing the quantity of the gas pumped; furthermore,they are independent of the rate of gas injection [6,7]. On the contrary, the pumping speed for H_2 displays a much smaller decrease and is dependent on the rate of injection.

Compared with the St101 NEG, which shows no pumping for activation temperatures below about 600° C, the St 707 NEG already provides appreciable pumping after 300° C activation, and reaches almost the maximum pumping speed after activation at 400° C. When exceeding this temperature, the pumping speed at first decreases and then again increases monotonically up to the maximum applicable heating temperature of 740° C.

To obtain more information on this very peculiar behaviour, the pumping speed for H_2 has been measured after activation at different increasing temperatures on the same sample, which was not exposed to ambient air between activations. After the last activation at 740° C the sample has been exposed to air and the same cycle of activation has been repeated.

The results of these measurements, shown in fig. 4, confirm the presence of a pumping speed maximum after 400° C activation, but also reveals an unexpected performance hysteresis, characterised by the absence of the maximum in the second sequence of activation cycles. This behaviour has been reproducibly observed on many samples, as well as for other gases (see figs. 5 and 6) showing that the St707 NEG does not reach the high pumping speed values hoped for after 400° C activation if it has been previously heated to higher temperatures.

In order to define the optimum baking cycle so as to obtain the highest pumping speed of the NEG through passive activation, the pumping speeds for H_2 have been measured after heating the NEG strip to 300° C, 350° C and 400° C for different periods of time. The results obtained (fig.7) indicate that for activation at 400° C the pumping speed decreases from the maximum value obtained after 45 minutes when longer activation times are applied. On the other hand the same maximum pumping speed is obtained in a stable manner at 300° C and 350° C for longer activation times. The latter temperature looks ideal because it allows the maximum pumping speed to be obtained after about 20 h, which represents the standard duration of a vacuum bakeout. However, the limited available experimental evidence does not exclude a possible long term pumping speed reduction consequent to many activation cycles at 350° C.

In real vacuum systems, and even more so in the vacuum systems of electron storage rings, where a strong outgassing is induced by synchrotron radiation, many different gas species are pumped simultaneously. It is therefore of practical importance to assess how the presence of a given gas influences the NEG pumping speed for another gas. In practice this information may be obtained during pumping speed measurements for a base gas by injecting small quantities of a sample gas. This procedure is described in more details in ref. 7. Fig. 8 shows the results obtained for the case of CO as base gas and H_2 and N_2 as sample gases. The pumping speed for CO is measured at regular intervals whereas the pumping speed for H_2 and N_2 are only measured a few times during the experiment. Similarly fig. 9 shows the results obtained for N_2 as base gas, in this case CO and H_2 are the sample gases. The results obtained with a lower activation temperature of 400° C are practically the same.

As already observed for the St101 NEG [6], pumping of H_2 does not affect the pumping speed of the St707 NEG for the other gases. Therefore the measurements carried out with H_2 as base gas are not reported here.

4. DISCUSSION

As already underlined when discussing the behaviour of the St101 NEG [6,7], gases heavier than H_2 do not diffuse from the surface into the NEG bulk at room temperature. Therefore the surface coverage increases with pumping time, and the pumping speed drops correspondingly. This decrease has been described in terms of decreasing conductance for gas molecules to reach adsorption sites on the surfaces of the voids inside the porous NEG layer. A detailed discussion of this process and its mathematical formulation are given elsewhere [6]. Surface blocking by heavy gas molecules is also responsible for the St707 behaviour when pumping gas mixtures, as already discussed for the St101 NEG [7].

In the case of H_2, room temperature diffusion is important and the NEG surface coverage (and hence its pumping speed) is defined by the competing effects of surface adsorption and diffusion into the bulk [15]. For this reason the pumping speed for H_2 is dependent on the pumping throughput and, in the case of gas mixtures, the presence of H_2 does not influence the pumping of other gases [7].

Besides these similarities, the St707 NEG provides a larger density of adsorption sites (as indicated by the larger pumping capacity) and a lower sticking coefficient for dissociatively adsorbed gases like N_2 and H_2, as shown by the lower pumping speed at low coverage (see fig. 3).

As already mentioned in the introduction, and illustrated by the measurements reported above, the peculiar feature of the St 707 NEG is its lower activation temperature.

The activation process of a gettering surface consists in the removal of the passive layer by thermally activated dissolution of the surface oxide layer and of the chemisorbed species into the getter bulk. Therefore a direct insight of the activation process may be obtained by monitoring the evolution of the surface composition while heating under UHV conditions.

Measurements of this type, carried out in various laboratories [16-21], indicate that a maximum Zr surface concentration of about 70% is achieved after 700° C heating. However a relevant difference has been observed when comparing the behaviour of NEG samples of different nature, i.e NEG strip (sintered powder) or alloy ingot. In the case of the strip the maximum Zr surface concentration is already obtained after heating at 500° C [19], whereas in the case of the ingot it increases more progressively up to the maximum temperature of 700° C reached in the experiment [20,21]. This difference has been attributed to a large concentration of crystallographic defects present in the powder, which provide easier diffusion paths for surface impurities and therefore allows removal of the passive layer at lower temperature. Whenever the annealing temperature of the alloy is exceeded, these defects disappear and higher temperatures are required for activation. Since after annealing

the room temperature pumping speeds for all gases are reduced, the surface defects seem also to enhance the molecular sticking coefficients [22].
This well documented plausible description is in good agreement with our results. Therefore we did not pursue our study further in this direction.

5. CONCLUSIONS

The experimental evidence produced in this study confirms that full activation of the St707 NEG may be reached after heating to 400° C for 45 minutes or to 350° C for about 24 h. Consequently this NEG is perfectly suitable for passive activation during bakeout of stainless steel vacuum systems.
Passive activation allows large amounts of NEG to be inserted into reduced volumes, thus providing large pumping speeds and very low ultimate pressures. For demonstration purposes the low 10^{-14} Torr range has been reached inside a 3 m long pipe. The modular nature of the proposed solution is such that this result may be extrapolated to vacuum systems of any length.
The present work unambiguously indicates that the benefit of the low activation temperature may be partially and irreversibly lost if the St707 NEG is heated to temperatures higher than 400° C for more than 1 h. This feature may spoil the NEG performance if this temperature is accidentally exceeded and/or following the accumulation of activation cycles. Although these risks did not materialise during the present study, they should not be ignored but rather be the object of more specific and detailed investigations.

References

[1] C. Benvenuti, Physica Scripta **T22**, 48 (1988).

[2] C. Benvenuti, Proc. 2nd European Vacuum Congress (EVC-2), Trieste, Italy, Vuoto **20**, 147 (1990),

[3] C. Benvenuti, Nucl. Instr. Meth. **205**, 391 (1983)

[4] LEP Vacuum Group, Vacuum **41**, 1882 (1990)

[5] P. della Porta, T. Giorgi, S. Origlio and F. Ricca, Proc. 8th Nat. Symp. AVS, (London 1962), p.229

[6] C. Benvenuti and F. Francia, J. Vac. Sci. Technol. **A6**, 2528 (1988)

[7] C. Benvenuti and F. Francia, J. Vac. Sci. Technol. **A8**, 3864 (1990)

[8] J. C. Schuchman, J. Vac. Sci. Technol. **A8**, 2826 (1990)

[9] C. Boffito, B. Ferrario, P. della Porta and L. Rosai, J. Vac. Sci. Technol. **18**, 1117 (1981)

[10] C. Benvenuti, P. Chiggiato and R. Kersevan, Proc. 2nd European Vacuum Congress (EVC-2), Trieste, Italy, Vuoto **20**, 307 (1990).

[11] C. Benvenuti and P. Chiggiato, Vacuum **44**, 511 (1993)

[12] P. Chiggiato, Sixth International Symposium on Electron Beam Ion Sources and their Applications EBIS 94 (Stockholm, June 20-23, 1994); to be published in Physica Scripta.

[13] E. Fischer and H. Mommsen, Vacuum **17**, 309 (1967)

[14] C. Benvenuti, J. M. Laurent and F. Scalambrin, Proc. 7th Int. Vac. Congr. and 3rd Int. Conf. Solid Surfaces, (Edited by R. Dobrozemsky, F. Rüdenaver, F. P. Viehböck and A. Breth), (Berger & Söhne, Vienna 1977), vol I, p. 113

[15] P. J. Knize and J.L. Cecchi, J. Appl. Phys. **54**, 3183 (1983)

[16] F. Meli, Z. Sheng, I. Vendel and L. Schlapbach, Vacuum **41**, 1938 (1990)

[17] I. Vendel and L. Schlapbach, J. Vac. Sci. Technol. **A11**, 539 (1993)

[18] Kenji Ichimura, Kan Ashida and Kuniaki Watanabe, J. Vac. Sci. Technol. **A3**, 346 (1985)

[19] Kenji Ichimura, Masao Matsuyama and Kuniaki Watanabe, J. Vac. Sci.

Technol. **A5**, 346 (1987)

[20] M. Sancrotti, G. Trezzi and P. Manini, J. Vac. Sci. Technol. **A9**, 182 (1991).

[21] J. Kovac, O. Sakho, P. Manini and M. Sancrotti, Surf. Interface. Anal. **22**, 327 (1994).

[22] G. A. Somorjai, Proc. 26th Yamada Conference on Surface as a New Material, (Osaka, Japan, 1990). Also in: Lawrence Berkeley Laboratory Note LBL 29277 (1990)

Figure captions

Fig. 1

Pumping speed of the St707 NEG after 45 min activation at 300° C and 400°C as a function of the pumped quantities of CO, N_2 and H_2.

Fig. 2

Pumping speed of the St707 NEG after 45 min activation at 500° C and 600°C as a function of the pumped quantities of CO, N_2 and H_2.

Fig. 3

Pumping speed of the St707 and the St101 NEGs after 45 min activation at 740°C as a function of the pumped quantities of CO, N_2 and H_2.

Fig. 4

Pumping speed for H_2 of a new St707 sample (dots) and of a sample of this same NEG previously activated at 740° C and then exposed to air (squares) as a function of the activation temperature (duration of activation time 45 min).

Fig. 5

Pumping speed for N_2 as a function of the pumped quantity of a St707 NEG sample previously activated at 740° C and then exposed to air, after 45 min activation at 300° C, 450° C and 600°

Fig. 6

Pumping speed for CO as a function of the pumped quantity of a St707 NEG sample previously activated at 740° C and then exposed to air, after 45 min activation at 300° C, 450° C and 600° C.

Fig. 7

Variation of the initial pumping speed for H_2 of a St707 NEG as a function of the heating time and for various heating temperatures.

Fig. 8

Variation of the measured pumping speed for H_2 , N_2 and CO as a function of the adsorbed quantity of CO.

Fig. 9

Variation of the measured pumping speed for H_2 , N_2 and CO as a function of the adsorbed quantity of N_2.

FIGURES

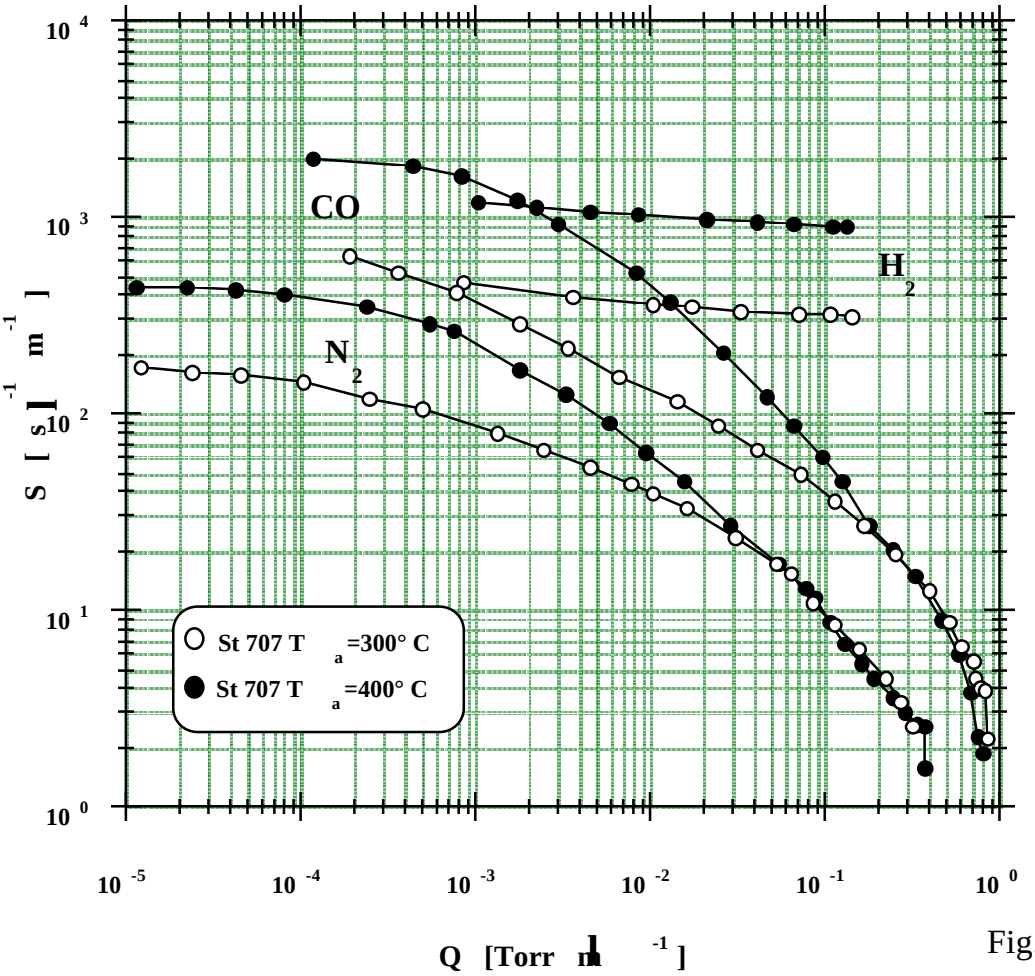


Fig. 1

Fig. 2

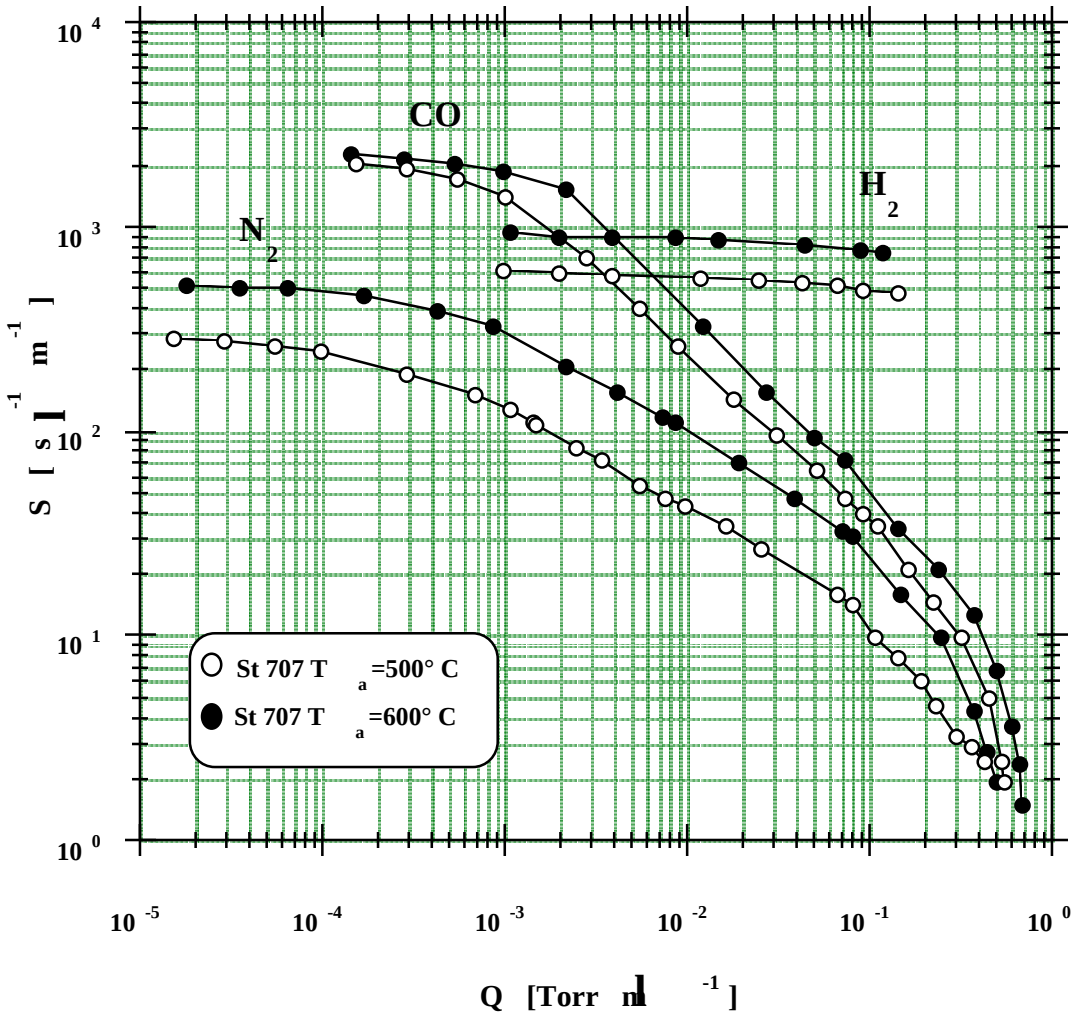

CO
H2
N2
St 707 Ta=500° C
St 707 Ta=600° C
S [s-1 m-1]
Q [Torr l s-1]
10 4
10 3
10 2
10 1
10 0
10 -5
10 -4
10 -3
10 -2
10 -1
10 0

Fig. 3

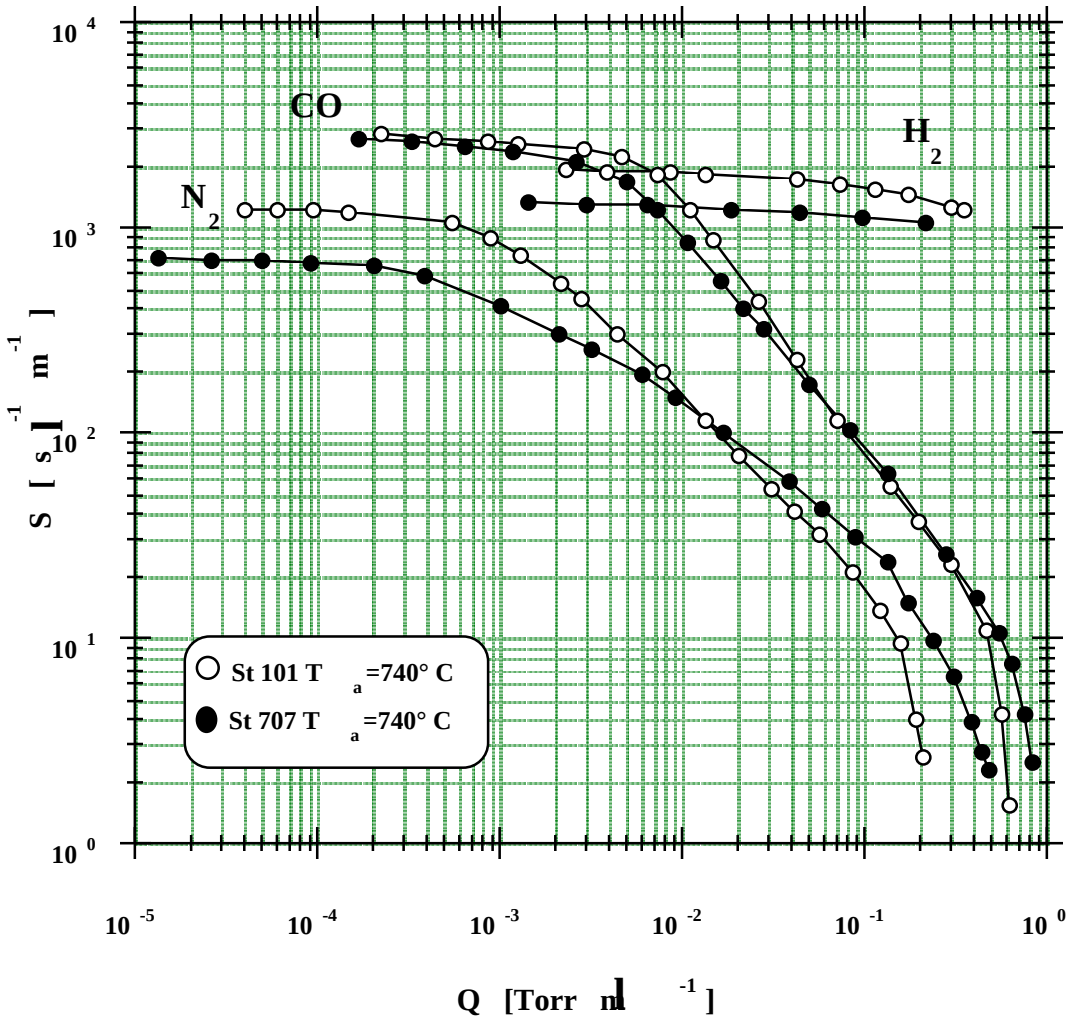

CO
H2
N2
St 101 Ta=740° C
St 707 Ta=740° C
S [s-1 m-1]
Q [Torr ml-1]
10 4
10 3
10 2
10 1
10 0
10 -5
10 -4
10 -3
10 -2
10 -1
10 0

Fig. 4

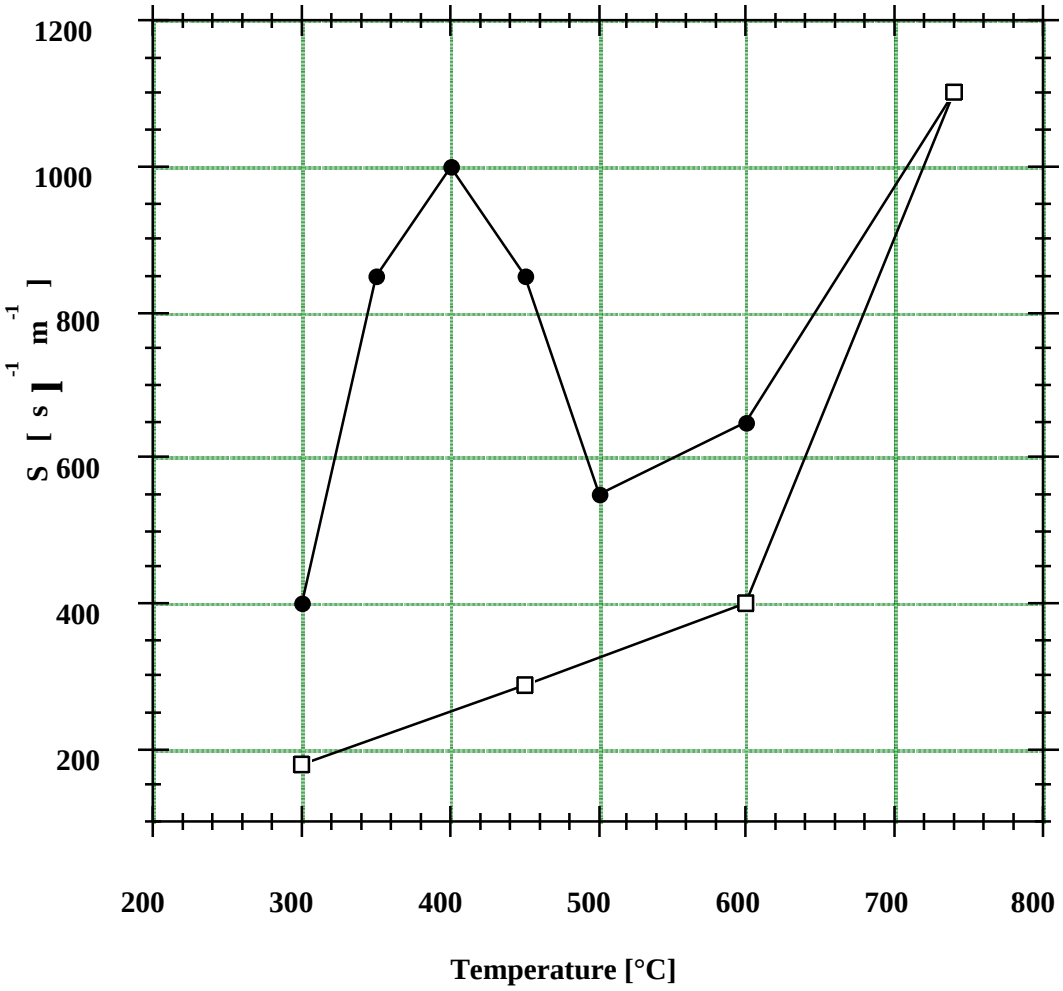

1200
1000
800
600
400
200
S [s] [m]
-1
-1
200
300
400
500
600
700
800
Temperature [°C]

Fig. 5

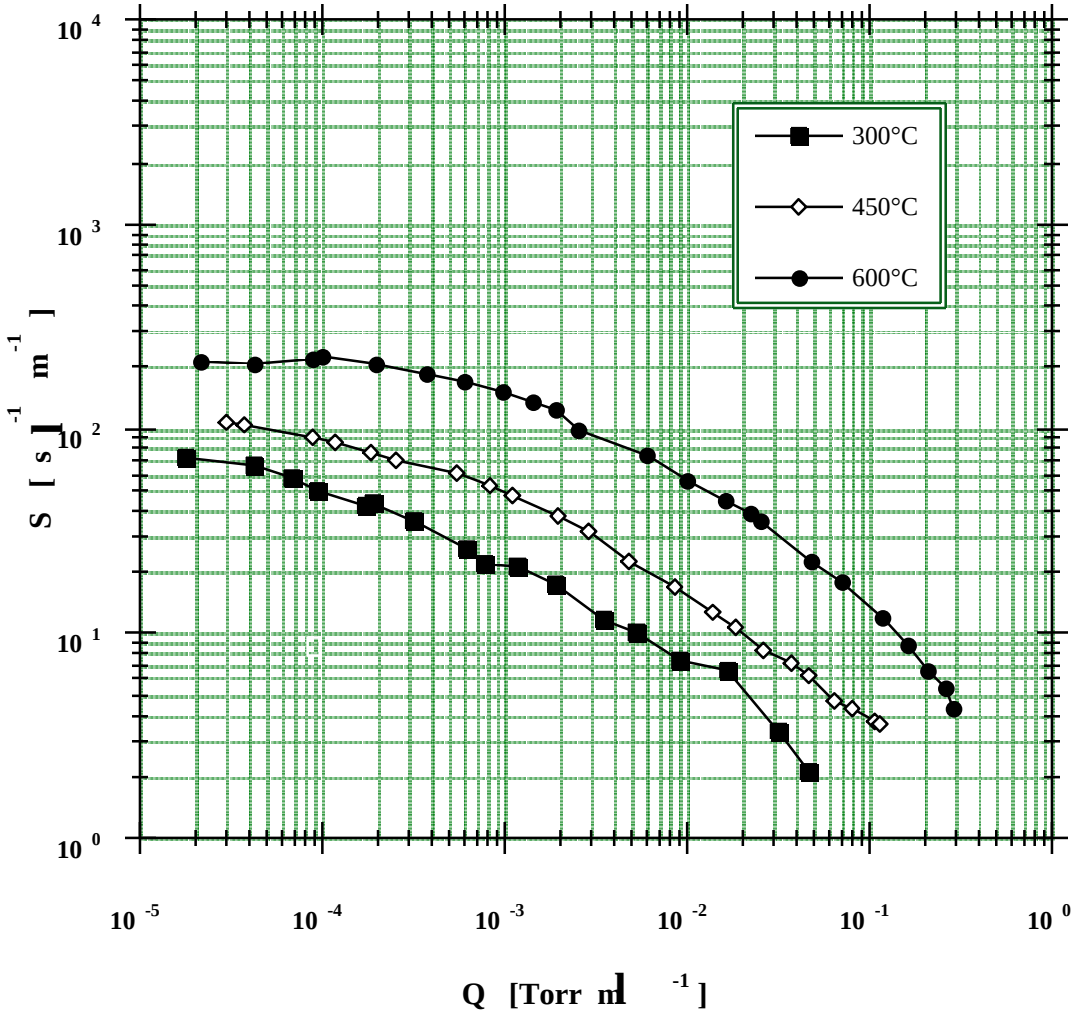
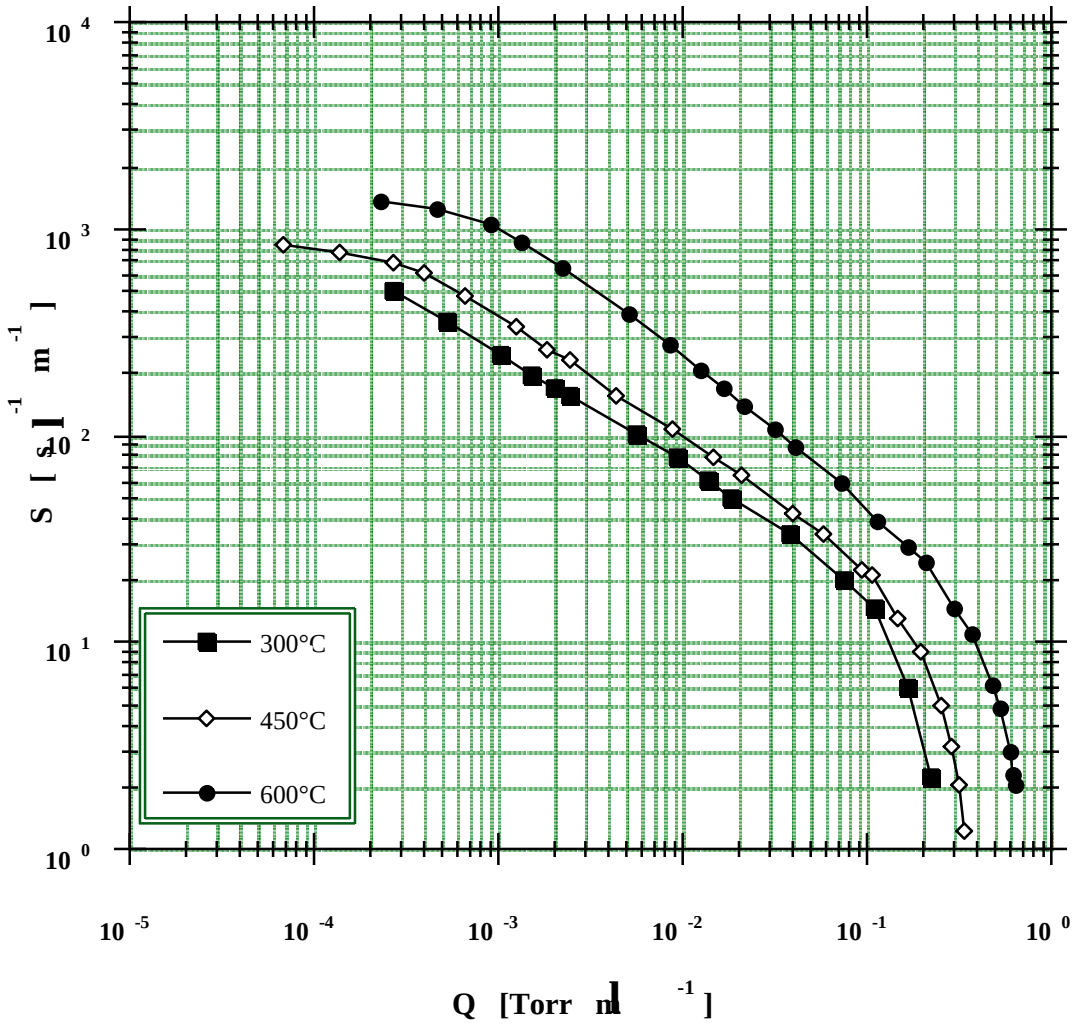

300°C
450°C
600°C
10 4
10 3
10 2
10 1
10 0
S [s -1 m -1]
10 -5
10 -4
10 -3
10 -2
10 -1
10 0
Q [Torr ml -1]

Fig. 6


10 4
10 3
10 2
10 1
10 0
S [l s -1 m -1]
10 -5
10 -4
10 -3
10 -2
10 -1
10 0
Q [Torr l m -1]
300°C
450°C
600°C

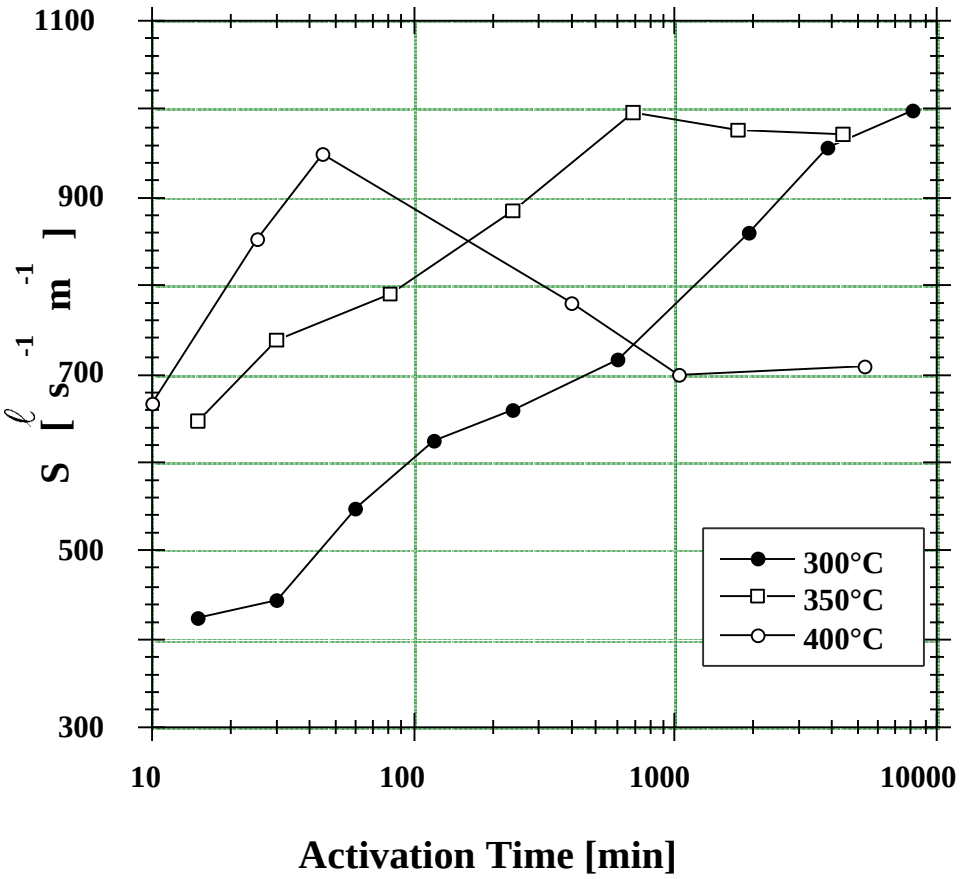

1100
900
700
500
300
10
100
1000
10000
S [s m]
-1
-1
300°C
350°C
400°C
Activation Time [min]

Fig. 8

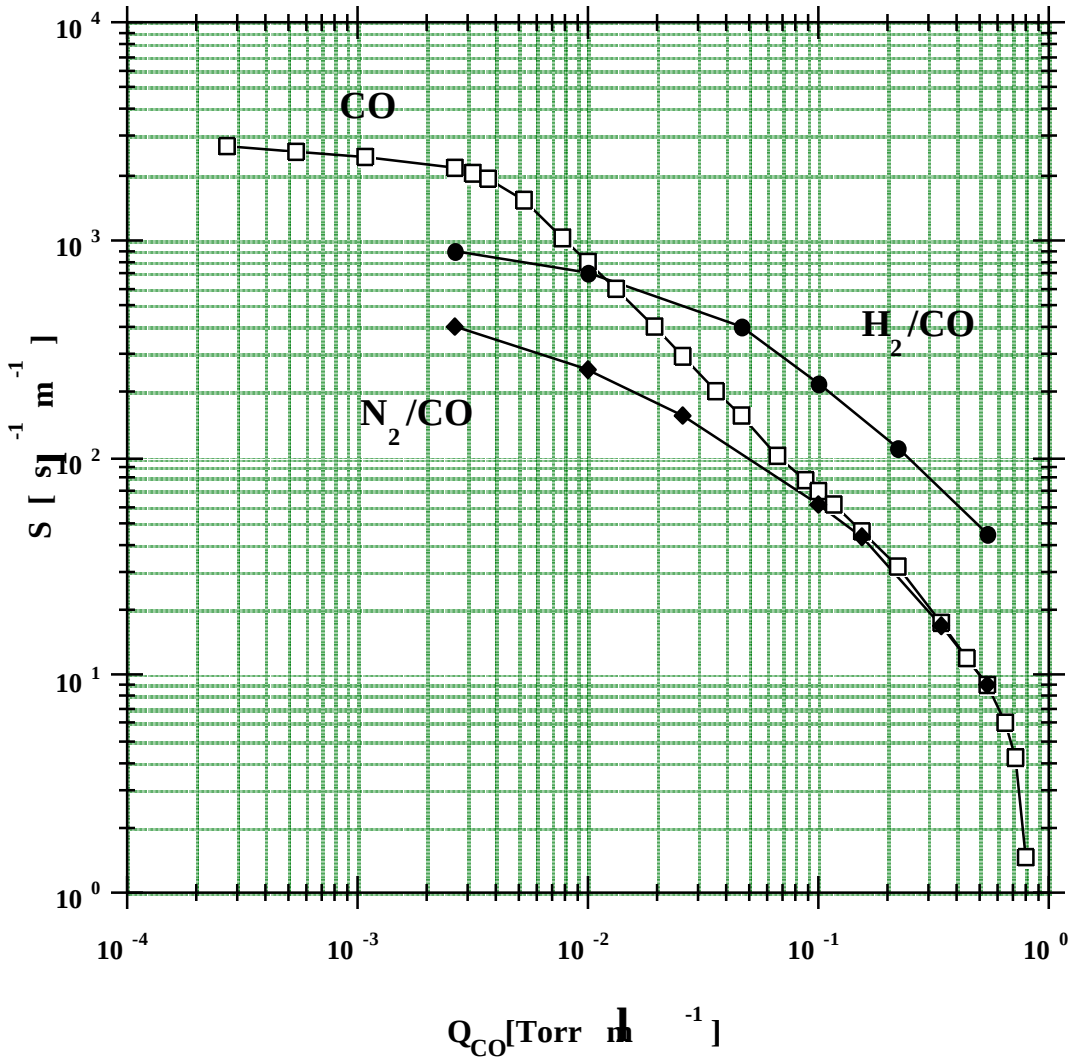
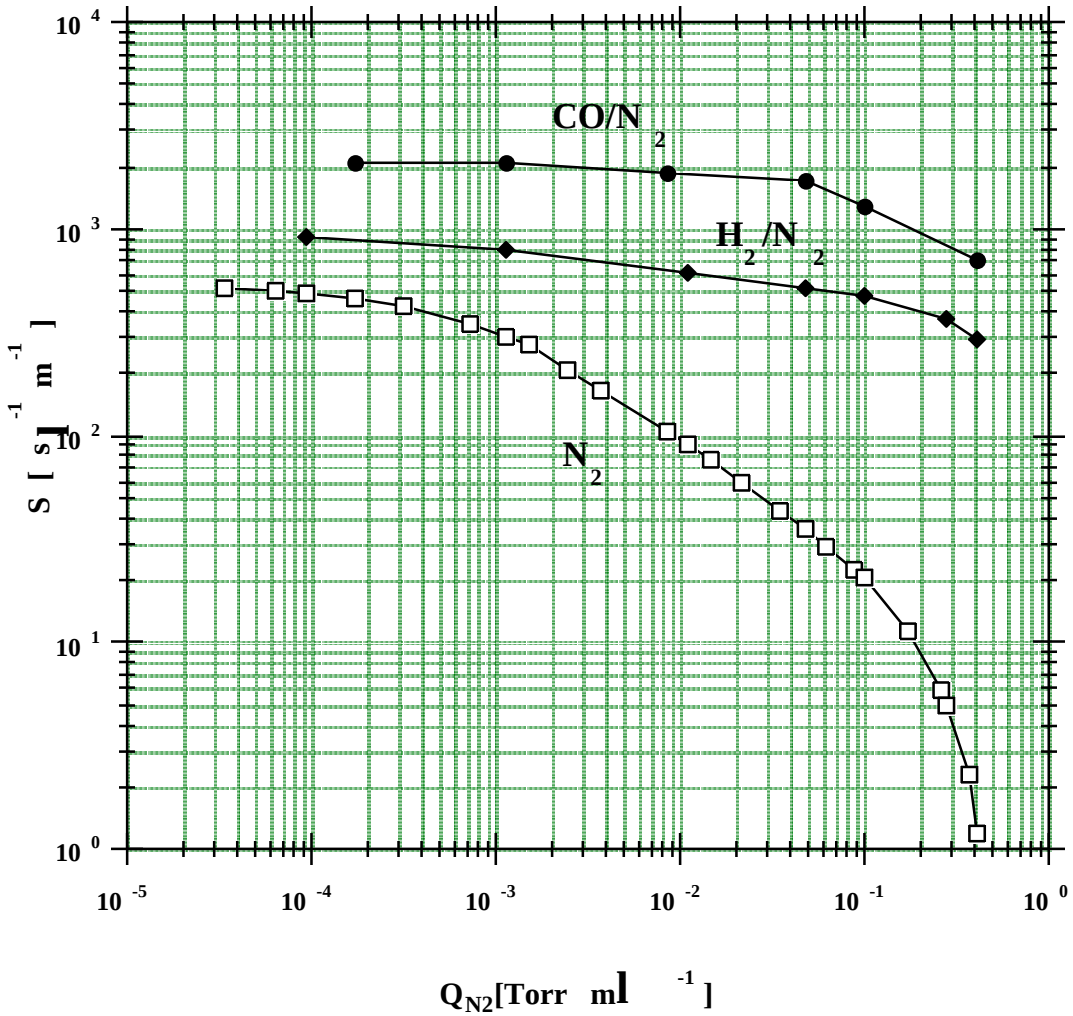

CO
H2/CO
N2/CO
S [s-1 m-1]
QCO[Torr ml -1]
10 4
10 3
10 2
10 1
10 0
10 -4
10 -3
10 -2
10 -1
10 0

Fig. 9


CO/N2
H2/N2
N2
S [s-1 ml-1]
QN2[Torr ml-1]
10 4
10 3
10 2
10 1
10 0
10 -5
10 -4
10 -3
10 -2
10 -1
10 0