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ROOM TEMPERATURE PUMPING CHARACTERISTICS FOR GAS MIXTURES

OF A Zr-Al NON-EVAPORABLE GETTER

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Abstract

The main pumping for the vacuum system of the Large Electron Positron collider (LEP), which has been commissioned at CERN in the Geneva area, is achieved by a linear getter pump. In distinction with the usual operating conditions of Non-Evaporable Getter (NEG) pumps, which consist in maintaining the getter hot to continuously diffuse into the getter bulk the gases adsorbed on its surface. the LEP pump will be kept at ambient temperature and heated only intermittently. This difference has required a study on the behaviour of a NEG pump under these unusual operating conditions, which result in a progressive reduction of pumping speed with increasing quantity of the gas adsorbed. It was found that the pumping speed reduction may be described in terms of a progressive saturation of the NEG surface inside the cracks and porosities which are present in the getter film thickness. The formulation developed permits one to reconstruct the pumping curves of a NEG, provided that a few basic geometrical and physical quantities are known. This description, which had been applied to individual gases in a previous paper, is extended here to the case in which mixtures of different gases are pumped.

1. INTRODUCTION

A non-evaporable getter (NEG) strip subtended along the inside of a vacuum chamber may provide an economic distributed pump of large pumping speed and capacity, particularly suitable for use in the conductance limited vacuum systems of particle accelerators[1]. A linear NEG pump has been adopted for the Large Electron Positron collider (LEP) which has been commissioned at CERN in the Geneva area[2,3].

Use of such a pump for a particle accelerator implies, however, abandoning the traditional operating mode where the getter is kept hot while pumping[4]. Heating is required to diffuse into the getter bulk the molecules which are continuously adsorbed on its surface and which would otherwise progressively reduce its pumping speed. In the case of LEP. the NEG strip is electrically insulated with respect to the 11 m long vacuum chamber, and it is accessible for heating by Joule effect via electrical feedthroughs installed at both ends of each chamber. Continuous heating, however, would not be feasible, because the electric-magnetic effects of a current flowing in the getter would upset the circulating electron beams, and also because it would yield an excessive H_2 pressure[4] and require excessive power. NEG surface cleaning, therefore, may be achieved only by intermittent heating to be supplied, in the absence of beam, whenever the NEG pumping speed decreases to below the minimum acceptable value for the considered application.

Because of the lack of experience for this operating mode, the room temperature behaviour of the chosen NEG in the presence of various gases and gas mixtures was studied in detail. The purpose of the study was to ascertain how frequently the NEG should be heated in LEP operating conditions and, possibly, to optimise the relevant NEG production parameters.

The pumping of individual gases has been the object of a previous note[5]: the pumping of gas mixtures is discussed in the present paper.

2. THE CHOSEN NEG AND THE PROPOSED PUMPING MODEL

The chosen NEG is a Zr-Al (16%) alloy bonded from a powder by cold pressing on a Constantan ribbon 30 mm wide and 0.2 mm thick. The alloy is

known by the trademark of St 101 and it is produced by SAES Getters (Milano, Italy)[6,7]. The manufacturer recommends heating under vacuum at about 700 °C (1 hour) for full activation, and continuous heating at about 400 °C during operation. The strip is coated on both sides and presents a narrow uncoated band on the edges, such that the active area is about 540 cm^2 per metre length.

The NEG surface is very rough. It is known that the very hard getter grains cannot be plastically deformed at the bonding pressure and that the total surface area exposed to vacuum after sintering is practically the same as that of the unbonded powder[8]. Therefore it may be assumed that voids of various size and irregular geometry are evenly distributed in the volume of the getter film. A direct confirmation of this has been also obtained by electron microscopy.

It has been shown[5] that the form of the adsorption curves for individual gases on this getter is a consequence of its physical structure. In order to obtain a mathematical description of the adsorption process going on inside the irregular voids, some simplifying assumptions have been introduced. It is assumed that[5]:

a) on a flat outer NEG surface a multitude of circular holes of equal diameter is present:

b) each hole represents the end aperture of a straight cylindrical void the diameter of which is the same as that of the holes and the length of which is equal to the getter film thickness.

Under these assumptions, the following adsorption process has been considered.

Initially, the gas molecules impinging on to the NEG are adsorbed either on the 'flat' outer surface or inside the voids. After adsorbing a certain amount of gas, pumping persists essentially inside the voids only. Saturation progresses inside the voids to a depth which is proportional to the quantity of gas pumped.

The pumping speed therefore becomes limited by the conductance of the void length that the molecules must travel to reach a still active surface.

In order to arrive at a quantitative formulation of this pumping mechanism, the following quantities have been introduced.

A_f = area of the 'flat' surface of 1 m of NEG strip (cm^2)

A_v = total area of the entrance orifices of the voids on 1 m of NEG strip (cm^2)

A = $A_f + A_v$ = 540 cm^2 = NEG coated surface of 1 m of NEG strip (cm^2)

n^2 = density of the voids per cm^2 of NEG coated surface

L = thickness of the getter coating (cm)

D = diameter of the voids (cm)

Q_0 = gas quantity needed to saturate the surface of 1 m of NEG strip which would not present any orifice on its surface (Torr 1 m^{-1})

Q_{sat} = gas quantity needed to saturate the surface of 1 m of NEG strip (Torr 1 m^{-1})

α_f = sticking factor on 'flat' clean surface

α_v = sticking factor at the entrance of the voids

S_f = pumping speed of the 'flat' outer surface of 1 m of NEG strip (1 $s^{-1}m^{-1}$)

S_v = pumping speed of the voids present on 1 m of NEG strip (1 $s^{-1}m^{-1}$)

S_0 = initial pumping speed of 1 m of NEG (1 $s^{-1}m^{-1}$)

C = conductance of an orifice of unit area (1 $s^{-1}cm^{-2}$).

With this notation the pumping speed of the NEG outer surface may be written as[5]:

$$S_f = \alpha_f A_f \, C \left(1 - \frac{Q}{Q_0(1-A_v/A)} \right) \qquad (1)$$

where in this case Q represents the gas quantity pumped on A_f, while S_v, according to the Knudsen formula for molecular flow, may be expressed for N_2 as:

$$S_v = \alpha_v \, n^2 \, A \frac{12.5 \, D^3}{\ell + 1.3 \, D} \qquad (2)$$

The gas quantity required to saturate A_f is:

$$Q_f = Q_0 \, A_f/A \qquad (3)$$

and the quantity required to saturate A_v to the depth ℓ is:

$$Q_v = n^2 \, \pi\ell \, D \, Q_0 \, . \qquad (4)$$

Therefore the total quantity of gas needed to saturate 1 m of NEG to the depth l is:

$$Q = Q_f + Q_v = (A_f/A + n^2 \pi l D) Q_0 \qquad (5)$$

and, for l = L,

$$Q_{sat} = (A_f/A + n^2 \pi LD) Q_0 \qquad (6)$$

If $Q \gg Q_0$, combining eq. (5) and eq. (6) gives:

$$l \simeq L Q_v/Q_{sat} \qquad (7)$$

Finally,

$$S_0 = (\alpha_f A_f + \alpha_v A_v) C \qquad (8)$$

Combining eq. (2) and eq. (4), under the approximation $l \gg D$ and $Q \gg Q_f$, gives:

$$S \simeq S_v = 3.44 \times 10^4 \alpha_v (A_v/A)^2 Q_0/Q_v \qquad (9)$$

The result is that a NEG may be completely characterized by three geometrical quantities (n^2, D, L) and three physical quantities, i.e. α_f, α_v and Q_0 which vary for different gases. For a given NEG the values of these quantities may be obtained by fitting eqs. (3) to (9) to the measured data[5].

Upon obtaining these values, it is possible to reconstruct the pumping curve for a given gas, for instance CO (Fig. 1)[5]. In this figure are shown the calculated $S_f(Q)$ and $S_v(Q)$, their combination $S(Q)$ and the experimental points. To obtain $S(Q)$, the injection of small CO quantities is simulated starting from zero coverage. Each injected quantity is subdivided in two parts. i.e. adsorbed on the outer surface and in the voids, proportionally to S_f and S_v at the coverages prior to the injection. After each injection, a new point on each of the curves $S_f(Q)$ and $S_v(Q)$ is defined, the coordinates of which are added to provide those of the corresponding point on the $S(Q)$ curve. Similar curves have been obtained also for N_2[5] while the pumping of mixtures of gases is discussed below.

3. EXPERIMENTAL PROCEDURE

Pumping speed measurements have been carried out by means of the equipment described in Ref. 5. It basically consists of a Fischer-Mommsen measuring dome[8] inside which a 25 cm long NEG sample may be heated by ohmic dissipation. The dome is bakeable and pumped by a turbomolecular pumping station. All samples have been cut from new NEG strips and replaced before giving any indication of performance deterioration consequent to gas pumping.

The test gases are H_2, CO and N_2. Previous measurements had shown that the NEG pumping of CO_2 may be assumed to be the same as that of CO in first approximation[5]. All the possible binary combinations of these three gases have been investigated. After an initial period during which two gases were injected simultaneously, it has been found preferable to inject minute amounts of a gas (sampling gas) while measuring the S(Q) curve of another gas (base gas). When the sampling gas was introduced, the injection of the base gas was stopped. In this way, the pumping speeds of both gases are obtained as a function of the pumped amount of the base gas. Obviously, the injected quantity of sampling gas must be small enough not to alter the pumping conditions of the base gas. For each gas combination the role of the two gases has been interchanged, in such a way that finally each of the three gases has served as base gas and sampling gas for the two others.

This procedure offers two important advantages. The first is that pumping speeds are obtained from total pressure measurements, while otherwise calibrated gas analysers should be used. The second is that it provides a better insight into the adsorption mechanism which takes place on the NEG surface, as it is shown in section 4.

4. RESULTS AND DISCUSSION

All samples are taken from strips delivered in 1986[5], which provide a porosity A_v/A ranging from 0.12 to 0.15. The pumping curves obtained for a typical sample are shown in Fig. 2.

By fitting Eqs. (1) to (9) to these curves, one obtains A_v/A = 0.13, D = 0.95 μm, n^2 = 1.9 x 10^7 voids cm^{-2}. The best fit for CO (Fig. 1) is

obtained for α_f = 0.39 and α_v = 1, while for N_2 α_f = 6 x 10^{-2} and α_v = 0.78. As already pointed out[5], this α_v value for N_2, constant and lower than 1, has not a simple physical justificaton. As a matter of fact, α_v should vary from a minimum initial value α_{vo} to unity for large N_2 quantity. Futhermore, α_f and α_{vo} should depend on each other in a way which may be defined by means of a Monte Carlo simulation programme. In the present case, one should take α_f = 0.1 and α_{vo} = 0.5 to reproduce the initial part of the S(Q) curve, but putting α_v = 1 for large Q values would lead to pumping speeds unambiguously larger than the measured ones. This crucial point will be discussed in paragraph 4.3.

Finally, it is worth recalling[5] that adsorbed H_2 diffuses away from the surface into the getter and therefore the pumping speed for this gas is quantity independent. However, for injection rates larger than about 10^{-5} Torr l s^{-1} m^{-1}, $S(H_2)$ becomes dependent on the rate of injection because the diffusion is not fast enough to cope with the rate of H_2 arrival. This results in a progressive accumulation of H_2 near the NEG surface, which in turn produces the decrease of pumping speed shown in Fig. 2 (here the injection rate is about 6 x 10^{-4} Torr l s^{-1} m^{-1}). At low H_2 injection rates α_f = 4.4 x 10^{-2} and α_{vo} = 0.35. This point will be taken up again in paragraph 4.2.

4.1 Hydrogen as Base Gas

Due to H_2 diffusion, pumping of even larger H_2 quantities does not affect the subsequent pumping of N_2 and CO. The measured pumping speeds for these gases are the same after H_2 injection as for a freshly activated NEG sample.

4.2 CO as Base Gas, H_2 as sampling gas (S(H/CO))

The situation resulting from H_2 injection on a surface partially saturated with CO is depicted in Fig. 3. This figure shows that H_2 pumping is markedly inhibited by preadsorption of CO. The S(H/CO) curve becomes parallel to, and remains about a factor 4 higher than, the S(Q) for CO at large CO coverage.

The S(H/CO) curve may be calculated in the following way. Any injected amount Q of CO is decomposed in the usual manner[5] into Q_f and Q_v. These values define a percentage of A_f and a length of the cylindrical voids where the H_2 pumping is fully inhibited. The H_2 pumping speeds S_f and S_v may then be calculated using the proper values of α_f and α_v for H_2. Finally, the total H_2 pumping speed for the considered amount of adsorbed CO is obtained by adding S_f and S_v.

The result of this exercise is shown in Fig. 4. Remarkable agreement with the experimental curve is obtained by taking $\alpha_f = 4.4 \times 10^{-2}$ and assuming that α_v increases from an initial value of 0.35 to 1 for large CO coverage. Both the initial value of α_v and its evolution have been derived from α_f making use of the Monte Carlo calculations carried out by C.G. Smith and G. Lewin[10].

As already observed for N_2[5], also for H_2 the assumption of "single site" adsorption results in a bump in the calculated curve, which departs from the experimental curve in its central region. Agreement is restored by assuming that two adsorption sites (p=2) are needed to pump a H_2 molecule. This is not surprising since H_2 diffusion at room temperature implies dissociative adsorption, i.e. it must involve in the process a number of adsorption sites at least equal to the number of atoms present in the H_2 molecule.

In spite of the good fit obtained in Fig. 4, one could question whether a similarly good fit could not also be obtained with constant α_v. The answer is given in Fig. 5. If one choses the α_f and α_v values which provide good fit at low coverage, a large discrepancy at high coverages is obtained at constant α_v. To restore a good fit at large coverage, α_v should be doubled. However, in this case the fit at low coverage would be lost, unless one takes $\alpha_f = 0$, which is physically unrealistic.

In conclusion, these results provide an important confirmation of the proposed pumping model, according to which the NEG pumping speed at large coverages is conductance limited and α_v increases with coverage and finally becomes equal to one. Why this does not happen for N_2 is still an open question.

4.3 CO as Base Gas, N_2 as Sampling Gas (S(N/CO))

The situation obtained in this case is depicted in Fig. 6. Since N_2 and CO have the same molecular mass, they should experience the same conductance. At large CO coverage, S(N/CO) should therefore coincide with the S(Q) curve for CO.

This is precisely what has been found experimentally (see Fig. 6). Not surprisingly, if one calculates it in the usual way (as described for H_2 in paragraph 4.2), the S(N/CO) curve coincides perfectly with the S(Q) for CO at large coverage when assuming $\alpha_f = 0.1$ and α_v ranging from an initial value of 0.5 to a final value of 1.

Why in the case of N_2 alone α_v does not reach unity at large N_2 coverage[5] still remains an open question. A physical justification of this discrepancy may be found in the over simplified assumption, in the pumping model developed, of the existance of a sharp saturation front in the NEG voids. A more realistic view would consist in assuming that the saturation is smeared out over an appreciable length. For gases which undergo single site adsorption, the partial extension to a lower depth of the saturation front is compensated by the adsorption on the free sites left behind. For N_2 molecules which require to be adsorbed many adjacent free sites and present low α_f[5], the whole region where some adsorption has taken place is likely to provide a very reduced pumping action. In practice, this effect would act as a displacement of the saturation front further down in the voids, resulting in a smaller conductance. In order to be compatible with the observed behaviour, the displacement of this "effective" saturation front should be proportional to the amount of gas injected. In this case a translation of the S(Q) curve would be produced in a logarithmic scale diagram. A confirmation of this hypothesis could be obtained by a full Monte Carlo computation, which, for the time being, has not yet been carried out.

4.4 N_2 as Base Gas

The observations carried out using H_2 and CO as base gases are consistent with a picture which links the inhibition of adsorption to the permanence of the base gas on the surface. Results obtained using N_2 as base gas indicate that this simple rule is not obeyed in certain cases.

As Fig. 7 shows, S(CO/N) is completely unaffected by preadsorbed N_2, although this gas does not diffuse in from the surface. Continuous monitoring of mass 14 during CO injection indicates that no N_2 is released when CO is adsorbed. The evidence is that N_2 is adsorbed, it does not diffuse nor is it displaced by CO, but it does not inhibit the pumping of this latter gas.

This behaviour, already observed for a Zr surface[11] has led to the hypothesis that N_2 is adsorbed underneath the first monolayer of the surface, which therefore remains free for adsorbing another gas.

Using H_2 as sampling gas brings about another complication. As shown in fig. 8, H_2 adsorption is affected by the preadsorption of N_2 in a still different manner, i.e. it is only partially inhibited. In all other cases, the inhibition was either complete or non existent. The measurements are consistent with 70% surface blocking, because at saturation with N_2 only 30% of the initial pumping speed for H_2 remains. Figure 8 indicates that good fit to the experimental data may be obtained by carrying out the calculation (as described in paragraph 4.2 for S(H/CO)) with the assumption that the part of the NEG surface which is covered by N_2 keeps 30% of its pumping speed for H_2. Understanding the causes of this phenomenon would require a specific investigation which exceeds the purpose of this study.

5. CONCLUSIONS

The pumping model which has been developed on the basis of results obtained on individual gases, also applies to gas mixtures. New experimental evidence reported in this note points out that the "anomalous" asymptotic value $\alpha_v = 0.8$ for N_2 probably has a non-trivial physical cause, which however for the time being remains unclear. Other peculiar properties of the N_2 adsorption have been observed which reveal a great complexity of this process. Full elucidation of this complexity exceeds the purpose of this study which has been motivated by the practical application of LEP pumping.

In this respect, the behaviour of N_2 has little relevance because the gases to be pumped by NEG in an electron accelerator or storage ring are mainly H_2, CO and CO_2. From a practical point of view, the key information is contained in the pumping speed curves of Fig. 3. These curves permit one to

estimate the evolution of the pressure inside the LEP vacuum chamber, provided that the integrated $CO+CO_2$ gas load and the actual degassing rates of H_2, CO and CO_2 are known.

It should not be forgotten, however, that these results are relative to new NEG strips of average performance. Pumping of various amounts of different gases will inevitably result in some NEG performance deterioration, as will be discussed in a future note.

ACKNOWLEDGEMENTS

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Figure Captions

Fig. 1 : Variation of pumping speed for CO as a function of the adsorbed quantity for a NEG belonging to a batch delivered for LEP in 1986. Measurements are represented by dots: full lines are the calculated curves. The porosity of the sample is 0.13.

Fig. 2 : Variation of the measured pumping speed for H_2 (triangles), CO (dots) and N_2 (crosses) as a function of adsorbed quantites for the same sample of Fig. 1. Full lines are a guide to the eye. The H_2 injection rate is 6 x 10^{-4} Torr l s^{-1} m^{-1}.

Fig. 3 : Variation of the measured pumping speed for H_2 (triangles) and CO (dots) as a function of the adsorbed quantity of CO. Full lines are a guide to the eye.

Fig. 4 : Variation of the measured (triangles) and calculated (full lines) pumping speed for H_2 as a function of the adsorbed quantity of CO. The experimental data are the same as in Fig. 3. Measurements of CO are omitted for clarity. S_f has been calculated for single site (p=1) and two sites (p=2) H_2 adsorption. S_v has been calculated with α_v ranging from 0.35 to 1.

Fig. 5 : Same as Fig. 4 with p=2 and constant α_v = 0.35.

Fig. 6 : Variation of the measured pumping speed for N_2 (crosses) and CO (dots) as a function of the adsorbed quantity of CO. Also represented (full line) the curve for N_2 calculated by assuming that α_v varies from 0.5 to 1. The line linking the CO measurements is a guide to the eye.

Fig. 7 : Variation of the measured pumping speed for CO (dots) and for N_2 (crosses) as a function of the adsorbed quantity of N_2. Full lines are a guide to the eye.

Fig. 8 : Variation of the measured pumping speed for H_2 (triangles) and N_2 (crosses) as a function of the adsorbed quantity of N_2. Triangles of different orientation represent results from two different samples. The upper full line is the calculated curve for H_2. The full line which links the N_2 measurements is a guide to the eye.
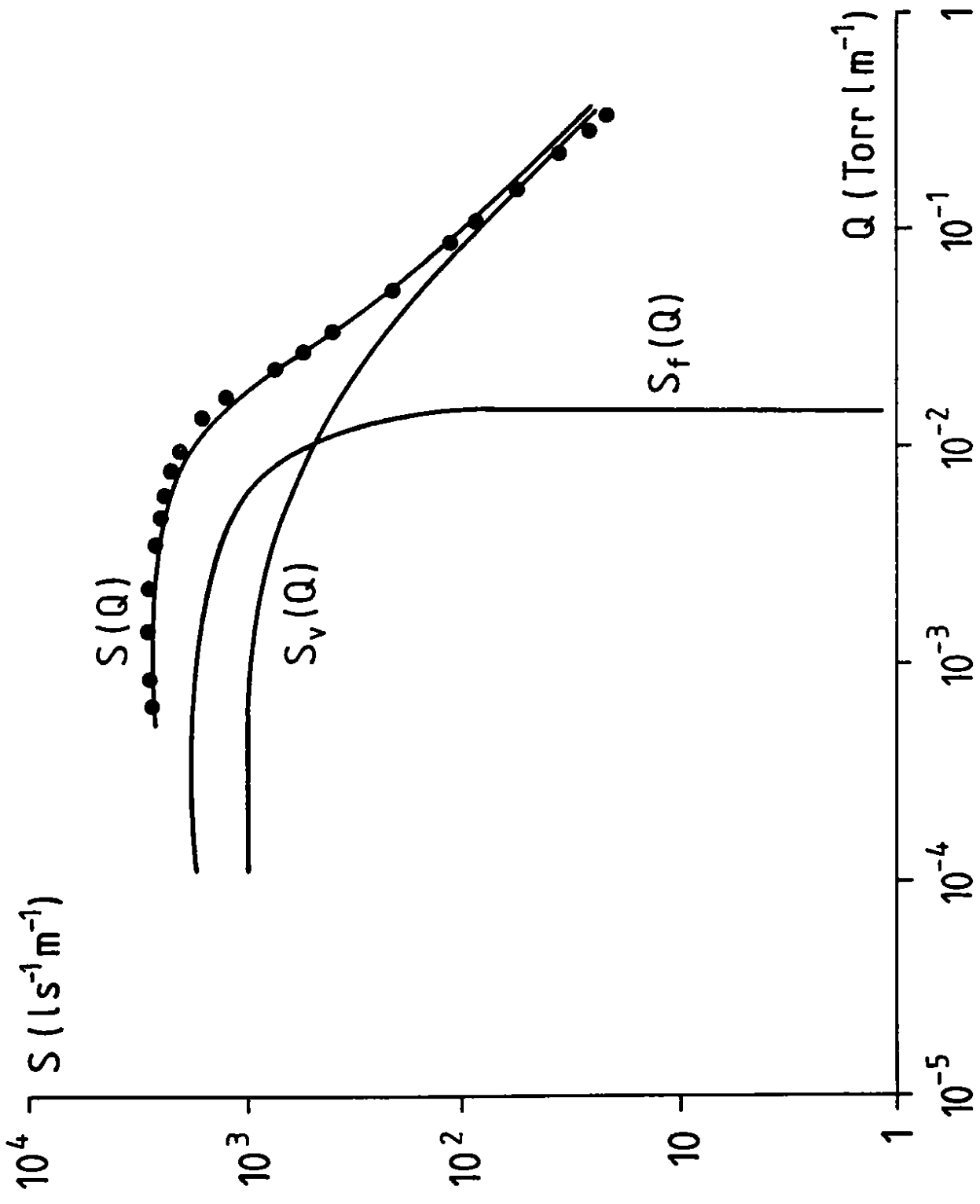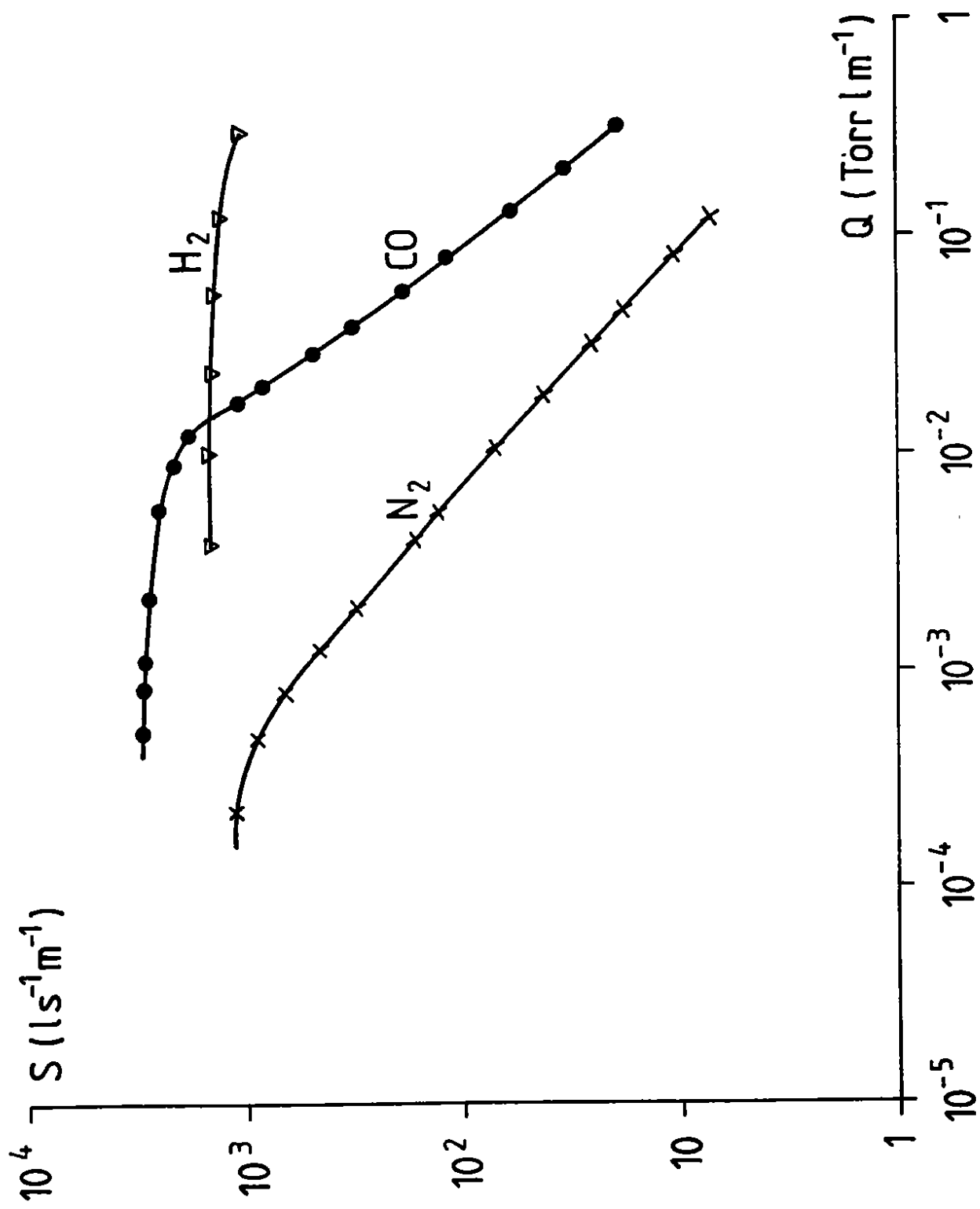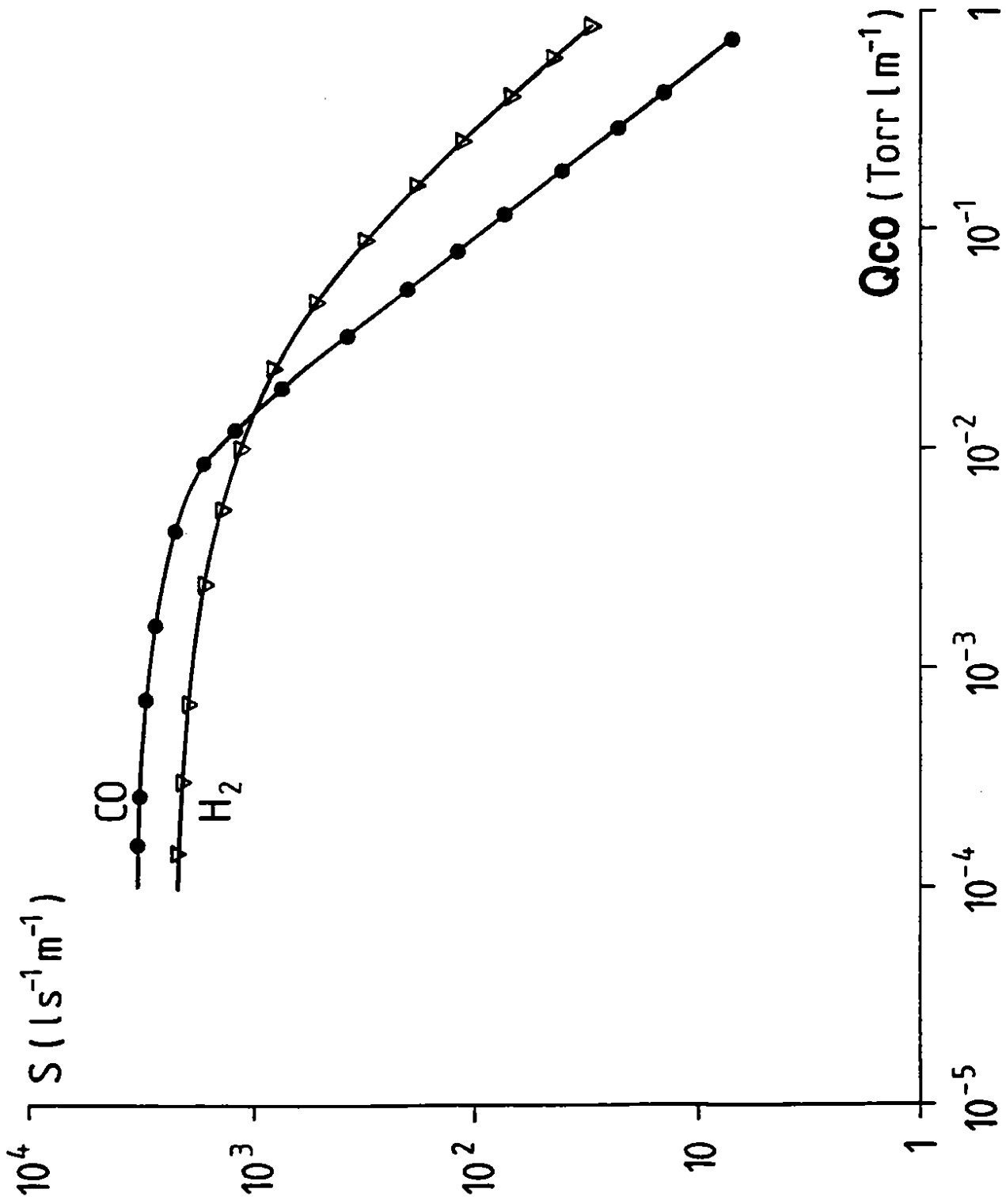
Fig. 1

S $(l s^{-1} m^{-1})$

10^4

10^3

10^2

10

1

10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 1

Q $(Torr \, l \, m^{-1})$
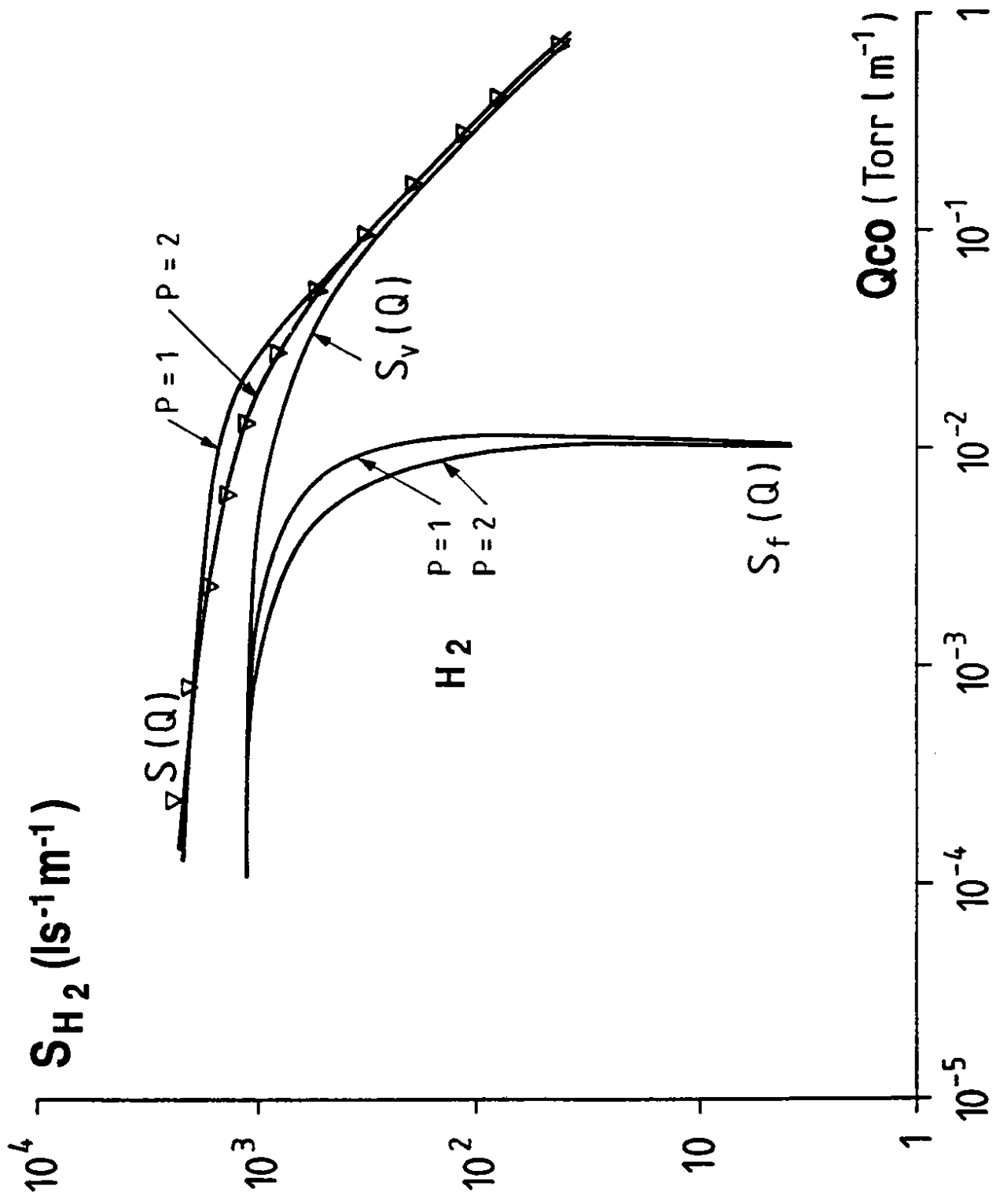
H_2

CO

N_2

Fig. 2

Fig. 3

S ($l\,s^{-1}\,m^{-1}$)

CO

H_2

Q_{CO} ($Torr\,l\,m^{-1}$)

Fig. 4

Fig. 5

Fig. 6

$S \, (l \, s^{-1} \, m^{-1})$

$Q_{co} \, (Torr \, l \, m^{-1})$

CO

N_2

Fig. 7

Fig. 8