

GETTER PUMPS

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1. Generalities
2. Evaporable getters
3. Non-evaporable getters
4. Thin film getter coatings

1. Generalities

- Molecular mean free path λ

$$\lambda = \frac{7.3 T}{10^{20} \pi r_0^2 p} \text{ cm}$$

T = absolute temperature (K)

p = pressure (Torr)

πr_0^2 = collision cross section (cm^2)

For N_2 $\pi r_0^2 = 4.26 \times 10^{-15} \text{ cm}^2$

at 295 K, $\lambda = 5 \times 10^3 \text{ p}$

[i.e. 5 cm at 10^{-3} Torr, or $5 \times 10^6 \text{ cm}$ at 10^{-9} Torr]

Molecular flow for $\lambda \gg$ wall distance

- Conductance and surface pumping

The conductance of C of an orifice (zero wall thickness approximation) may be expressed as

$$C = 3.64 (T/M)^{1/2} \ell \text{ s}^{-1} \text{ cm}^{-2}$$

With T = absolute temperature (K)
M = molecular weight

If all molecules impinging on a surface are captured, C represents the specific pumping speed S of the surface.

More generally

$$S = \alpha 3.64 (T/M)^{1/2} \ell \text{ s}^{-1} \text{ cm}^{-2}$$

where α is the sticking probability

$$(0 \leq \alpha \leq 1)$$

For $\alpha = 1$, $S \cong 44 \ell \text{ s}^{-1} \text{ cm}^{-2}$ for H_2
and $S \cong 12 \ell \text{ s}^{-1} \text{ cm}^{-2}$ for N_2
at room temperature

- Surface adsorption capacity

The monolayer capacity of an atomically flat surface is of the order of 5×10^{14} molecules cm^{-2} .

If this monolayer of gas is released in a spherical volume of 1 l (surface area $\sim 500 \text{ cm}^2$) the pressure increase would be 7×10^{-3} Torr.

Therefore

surface degassing is the main obstacle to achieving UHV conditions.

Conversely

under UHV conditions, surface pumping may be adopted.

- Surface saturation time (monolayer formation)

Combining surface pumping speed and capacity, the surface saturation time t_{sat} becomes

$$t_{\text{sat}} \approx 10^6 p \text{ seconds} \quad (p = \text{pressure in Torr})$$

when assuming

sticking probability = 1

atomically flat surface

ambient temperature

N_2 gas ($M = 28$)

Therefore, $t_{\text{sat}} \approx 1$ second at 10^{-6} Torr under these assumptions.

- **Sojourn time, desorption probability**

For a molecule adsorbed with a binding energy E on a surface at a temperature T the probability of escape v is

$$v = v_o e^{-\frac{E}{RT}} \quad (\text{Frenkel, 1924})$$

where v_o is an attempt frequency, of the order of the vibrational energy of the adsorbed molecules ($v_o \approx 10^{13} \text{ s}^{-1}$) and $R = 1.98 \times 10^{-3} \text{ kcal mole}^{-1} \text{ K}^{-1}$.

It is often more useful to use the reciprocal of this term, $\tau = \frac{1}{v}$, known as mean sojourn time or mean surface lifetime

$$\tau = \tau_o e^{\frac{E}{RT}}$$

Obviously, a surface provides a good pumping action when τ is much larger than the duration of the experiment.

Typical values of τ are given in table I [1]

Large τ values imply large E. However, surfaces providing low E values may display a useful pumping action when reducing the working temperature.

The Frenkel equation is often used in its logarithmic form. By plotting $\log P$ versus $1/T$ the measured pressure P is represented by a straight line the slope of which defines the energy of the considered adsorption process.

- Gas-surface binding energies

Two types of forces may bind a gas molecule to a surface.

Chemical forces

involving electrons, e.g. hydrogen bonding, covalent or metallic bonding, characterised by binding energies typically in the range of some eV per molecule or larger than 10 kcal/mole ($0.4 \text{ eV/molecule} \equiv 10 \text{ kcal/mole}$).

Van der Waals forces

of electrostatic nature, e.g. dispersion or polar forces, characterised by smaller binding energies, lower than 0.4 eV/molecule or 10 kcal/mole.

In the first case (chemical adsorption or chemisorption) long sojourn times are possible at room temperature (getter pumping).

In the second case (physical adsorption or physisorption) pumping requires surface cooling (cryopumping) because the mean sojourn time at room temperature is too short (see table I).

- **Definition of getters and getter pump types**

Getters are materials able to fix gas molecules on their surface in the form of stable chemical compounds.

To do so, their surface must be clean.

There are two ways of producing a clean gettering surface

- by "in situ" deposition of a fresh getter film
- by heating an oxidised getter to a temperature high enough to diffuse oxygen from the surface into the getter bulk.

In the first case, we speak about evaporable getters in the second case about non-evaporable getters (NEG) and the required heating temperature is called activation temperature.

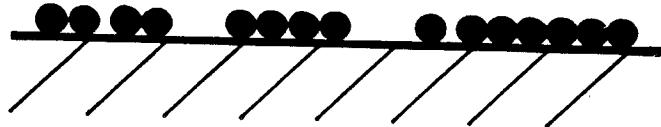
WHAT GETTERS ARE

1.



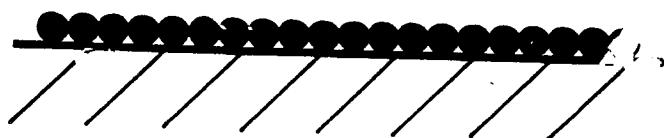
CLEAN
SURFACE

2.



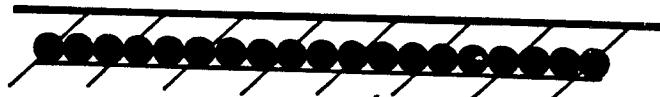
PARTIALLY
COVERED
SURFACE

3.



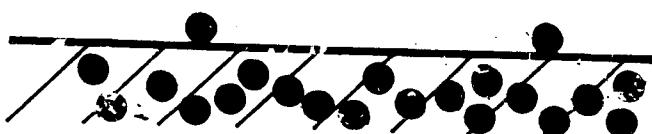
SATURATED
SURFACE

EVAPORABLE GETTERS (SUBLIMATION PUMPS)



**THE SATURED SURFACE IS
COVERED BY A FRESH LAYER**

NON-EVAPORABLE GETTERS (NEG)



**SURFACE CLEANED BY DIFFUSING
THE ABSORBED MOLECULES INTO
THE BULK (BY HEATING)**

CONTINUOUS OR INTERMITTENT HEATING

2. Evaporable getters

The two materials most widely used as evaporable getters are Barium and Titanium [2].

Barium is usually sublimated from a BaAl₄ alloy by heating at ~900°C. It is used for pumping vacuum sealed devices (electron tubes) and the sublimation is done in one single process before sealing. It is not used for UHV applications and will not be discussed here. For more details see ref. [3].

Titanium is the most widely used evaporable getter for UHV applications. It is usually sublimated from filaments made of Ti alloys (with Mo or Ta) heated up to 1500°C, temperature at which the Ti vapour pressure is about 10⁻³ Torr.

Titanium films provide sticking probabilities of 1 – 5 x 10⁻² for H₂ and 0.4 – 0.6 for CO at room temperature. Cooling to liquid N₂ temperature enhances these values to 0.1 – 0.3 for H₂ and about 1 for CO [4].

Other materials (Ta, Nb, V, Zr, Mo) have also been used, but their behaviour is not as good for various reasons [5].

Warning

Sticking probabilities reported in literature for a given gas-getter combination present a large spread. Besides possible experimental errors, this spread has two distinct causes, namely

- surface roughness
 - which may result in a large number of molecule-surface interactions, i.e. higher capture probability
- initial surface contamination
 - which may reduce the adsorption site density available for pumping; this effect is particularly important for measuring systems which provide a base pressure higher than about 10^{-9} Torr and/or when the sticking probability is measured at high pressures ($10^{-7} - 10^{-6}$ Torr).

At room temperature all gases but H₂ adsorbed by a Ti film remain on the surface, resulting in a progressive reduction of pumping speed. On the contrary, H₂ diffuses and its pumping is not affected by surface blocking.

On the other hand, the high (> 30 kcal/mole) binding energies prevent the desorption of gases adsorbed on Ti at practically allowed temperatures. Again H₂ represents an exception, since its lower binding energy (~ 20 kcal/mole) allows desorption by heating (see Table I).

The initial pumping speed of a Ti sublimation pump may be restored by a further sublimation process. The total pumping capacity is therefore very large and depends on the available amount of Ti in the filament.

The ultimate pressure of a Ti sublimation pump is in principle not limited; in practice it may be spoiled by the presence of rare gases and methane if an adequate pumping for this gases is not foreseen.

In conclusion, Ti sublimation pumps provide the following advantages and disadvantages:

Advantages

- large pumping speed
- large pumping capacity
- unlimited ultimate pressure
- compact
- inexpensive
- easily operated

Disadvantages

- no pumping for inert gases
- CH_4 production (?)
- localised pumping (particle accelerators !)

3. Non-Evaporable getters (NEGs)

NEGs are usually produced by fixing a powder of the getter material to a (metal) substrate by pressing, sintering or cathaphoresis [6]. After insertion in the system to be pumped, activation is carried out by heating.

Usually NEGs are alloys of the elements of the IV B columns of the Periodic Table, to which some of the actinides and rare earths may be added. Also Al is often added to increase the diffusivity of the adsorbed gases when heating. For more details on this subject, see [7].

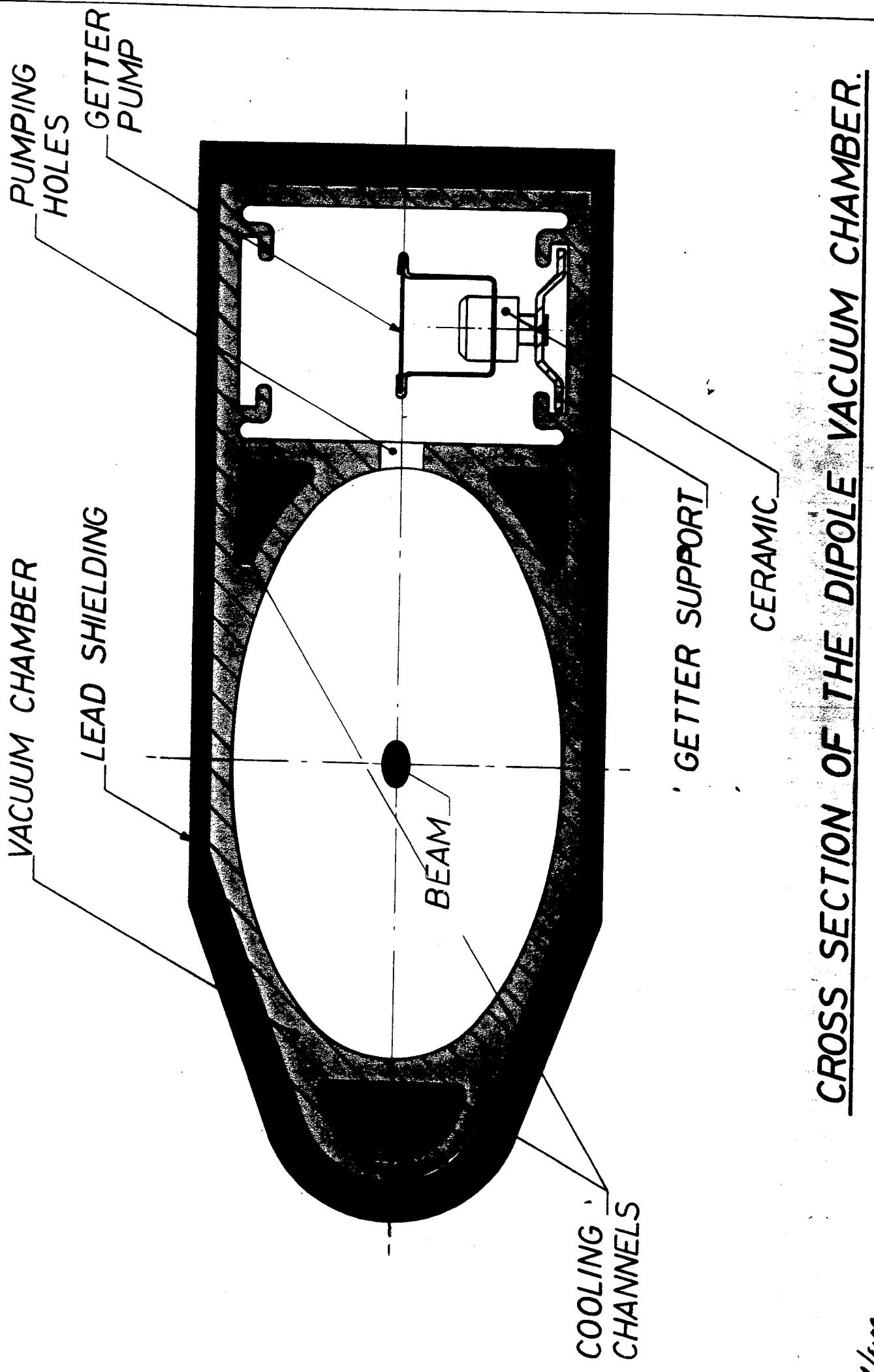
The performance of a given NEG is characterised by activation temperature, sticking probability, surface capacity, total pumping capacity (for H₂ and for heavier gases) and particle loss.

Since NEGs are highly porous (i.e. the small grains are in poor contact with the substrate), the danger of pyrophoricity imposes a lower limit to the activation temperature (350 - 400°C).

If compared to Ti sublimation pumping, NEG pumping presents the risk of powder peel-off (excessive heating or H₂ embrittlement) and a lower pumping capacity; however, NEGs may provide linear pumping and passive activation, if the activation temperature is compatible with the baking temperature of the chamber where the NEG is inserted.

This feature is particularly attractive because it removes the need of electric feedthroughs and powering/control systems and allows increasing the NEG surface and consequently its pumping speed.

All NEGs available on the market are produced by SAES Getters. We will consider here only the St 101 and the St 707, which are the best suited for UHV applications.



L. Lass
(May 1987)

Chamber Degassing rates

	Specific [Torr $\ell s^{-1} cm^{-2}$]	Total [Torr ℓs^{-1}]
H ₂	1×10^{-13}	1×10^{-8}
CH ₄	3×10^{-16}	3×10^{-11}

NEG Pumping Speeds (at zero coverage)

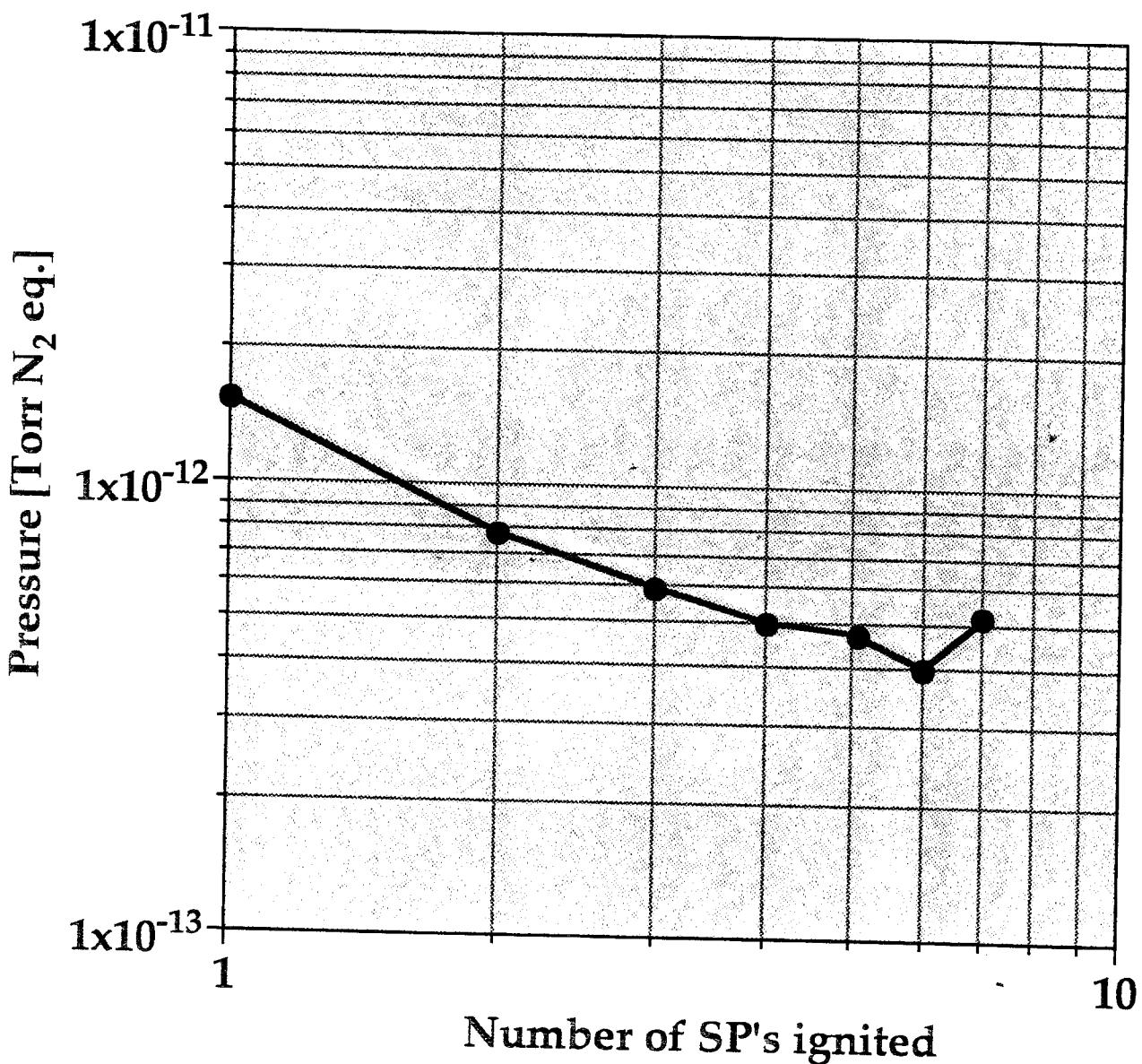
	Specific [$\ell s^{-1} m^{-1}$]	Total [ℓs^{-1}]
H ₂	2000	22000
CO	2800	30800
N ₂	1000	11000

Sputter-Ion Pumping Speed [ℓs^{-1}]

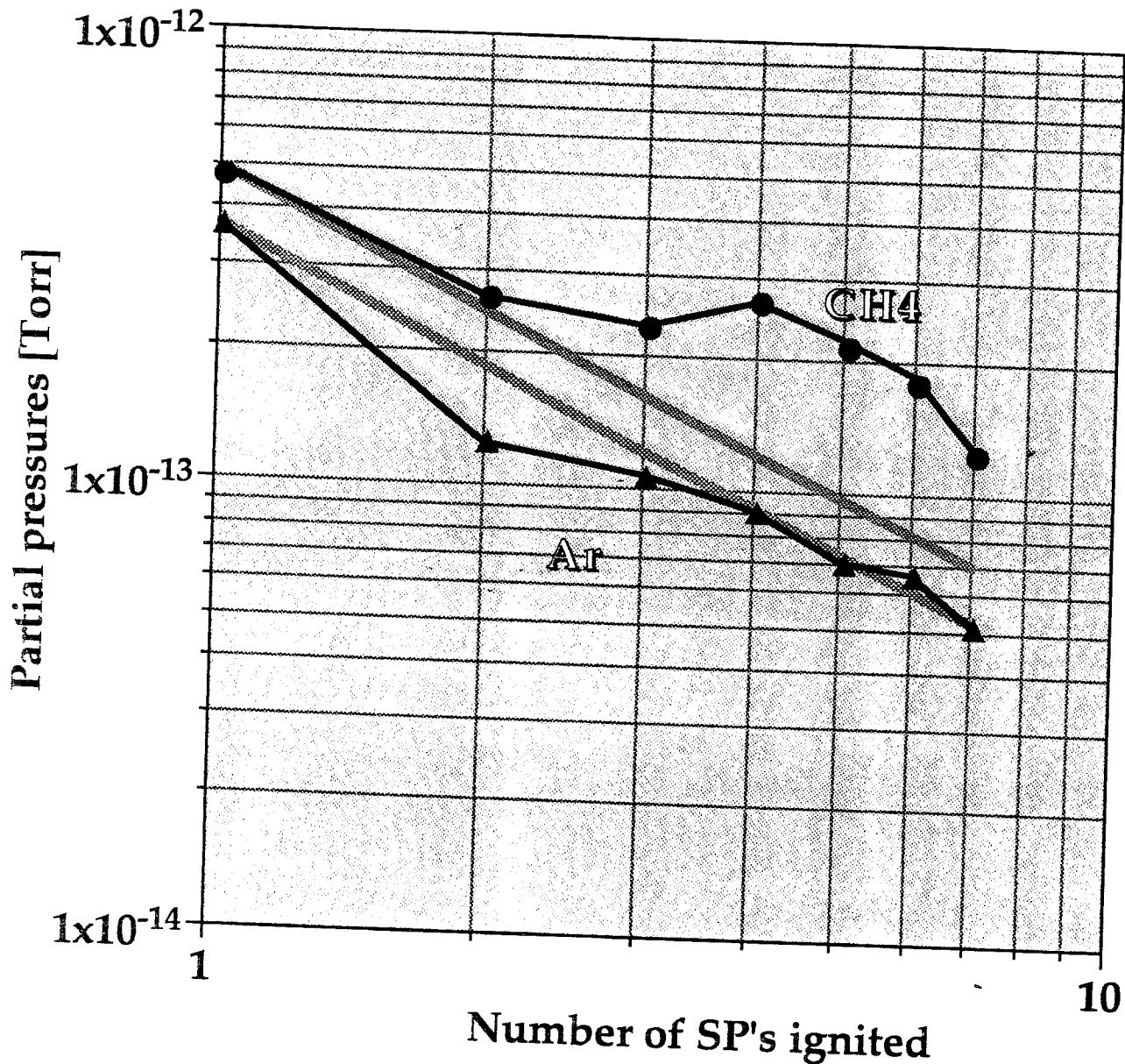
CH ₄	20
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Estimated ultimate Pressures [Torr]

H ₂	4.5×10^{-13}
CH ₄	1.5×10^{-12}



**Variation of the total pressure measured by the
Helmer gauge on chamber 1, as a function of the
number of SP's ignited, about 400 hours after
bakeout.**



Variation of the argon and methane partial pressures, as a function of the number of SP's ignited on chamber 2, about 400 hours after bakeout. The straight lines represent the partial pressures calculated under the assumption that all pumps provide, for the same gas, the same pressure independent pumping speed.

Both the St 101 and the St 707 have been extensively studied at CERN. The St 101 has been selected to provide the main pumping for the Large Electron Positron Collider (LEP) [13] (see Fig. 1). The main results are the following.

Ultimate pressure

A LEP chamber (12 m long, made of Al alloy, baked at 150°C pumped by St 101 and a sputter-ion pump of about 30 l s^{-1} speed reaches an ultimate pressure of about 2×10^{-12} Torr, mainly due to Ar and CH₄, gases not pumped by the getter. By adding 6 additional sputter-ion pumps a pressure of about 5×10^{-13} Torr (mainly H₂) is obtained [14] (see Fig. 2 and 3). Making use of the St 707 fully covering the inner walls of a stainless steel chamber, pressures in the low 10^{-14} Torr have been achieved after passive activation during 350°C bakeout [15] (see Fig. 4).

Pumping speed variation as a function of the amount of gas pumped

The S(Q) curves obtained at room temperature for the St 101 [16], represented in Fig. 5, indicate the importance of NEG porosity.

A mathematical model of the pumping process points out that, for a given gas load, the NEG pumping speed is proportional to the square of the porosity in the coverage range of practical interest. This model allows estimating the porosity from the S(Q) curves, in good agreement with the values obtained by direct porosity measurements.

The developed model also allows stipulating that on the St 101 CO is not dissociated (single site adsorption) while H₂ is dissociated (2 sites adsorption) as well as N₂, which however occupies 6 adsorption sites.

When gas mixtures are pumped [17], CO was found to inhibit the pumping of other gases, while N₂ has a small surface blocking effect and H₂ does not produce any blocking at all.

Pumping speed S

[$\ell s^{-1} m^{-1}$]

2000

1500

1000

500

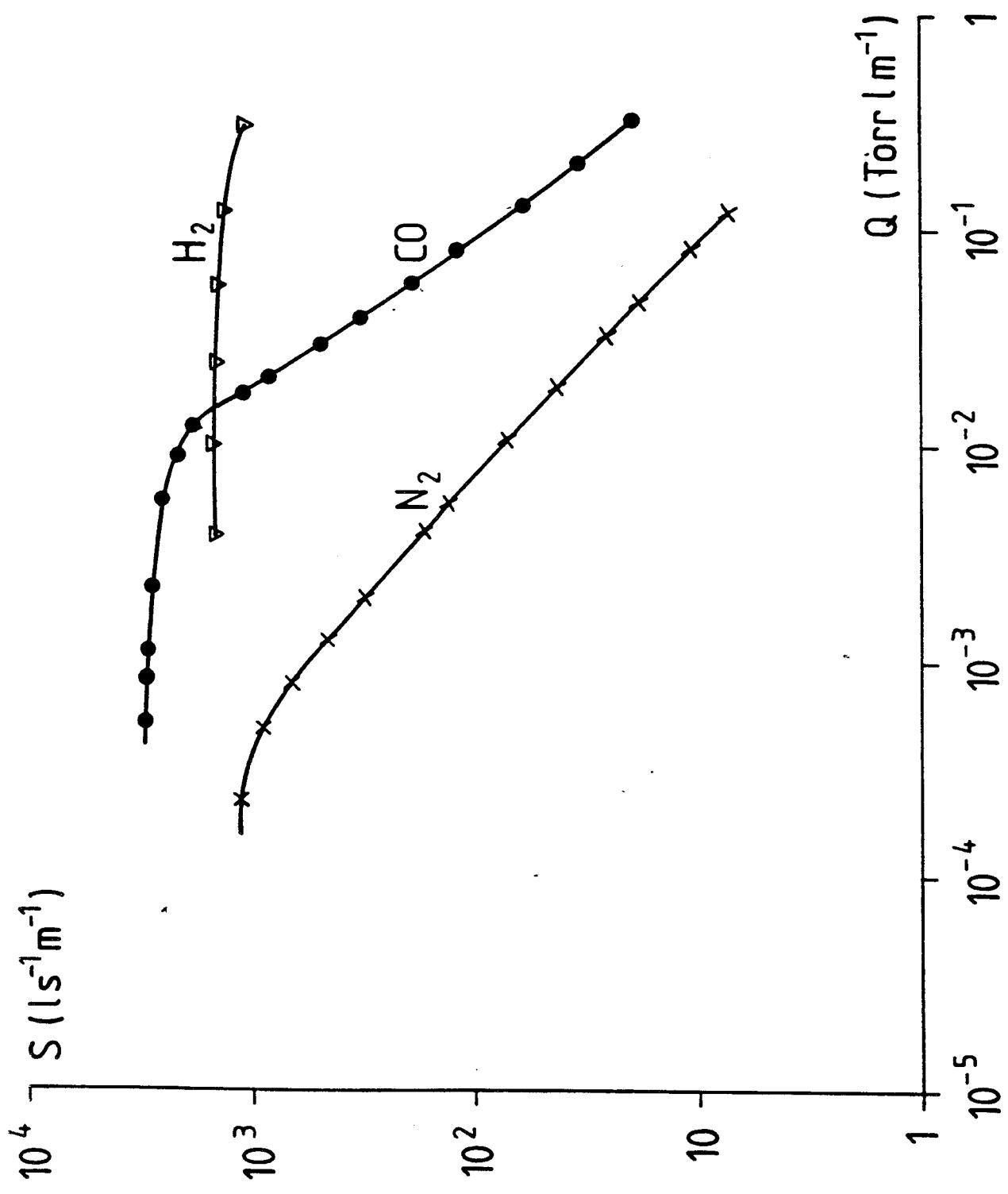
5×10^{-3}

10^{-2}

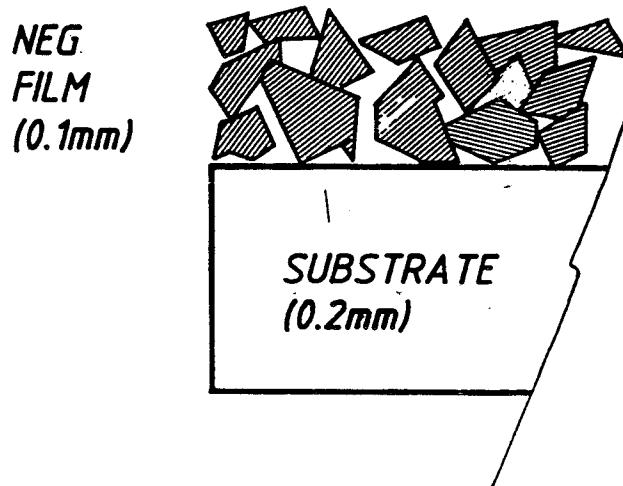
1.5×10^{-2}

Gas load Q [Torr ℓm^{-1}]

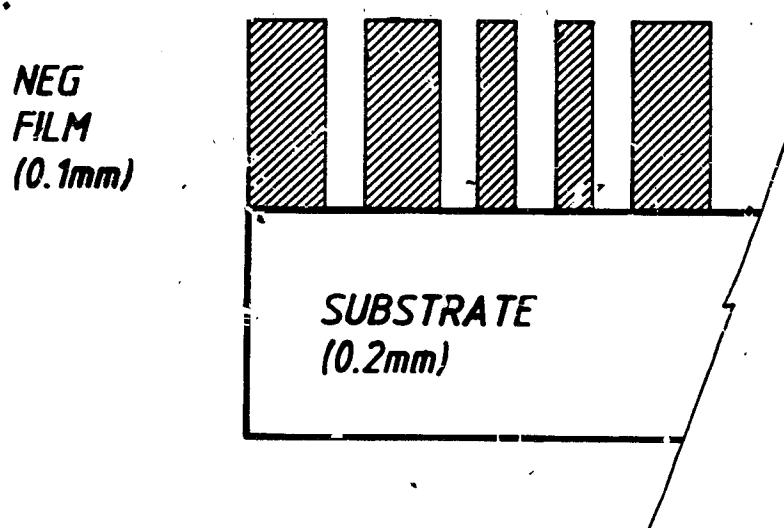
Q_o

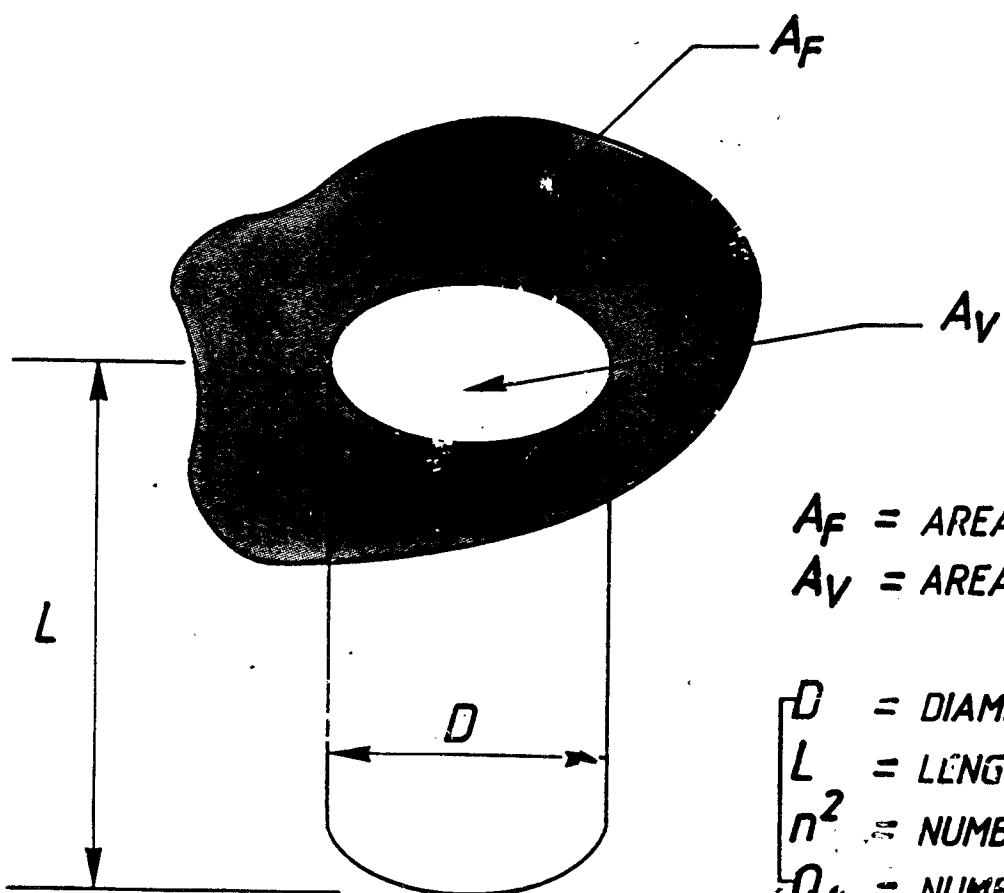


NEG STRUCTURE



SIMPLIFIED NEG STRUCTURE





A_F = AREA OF FLAT SURFACE

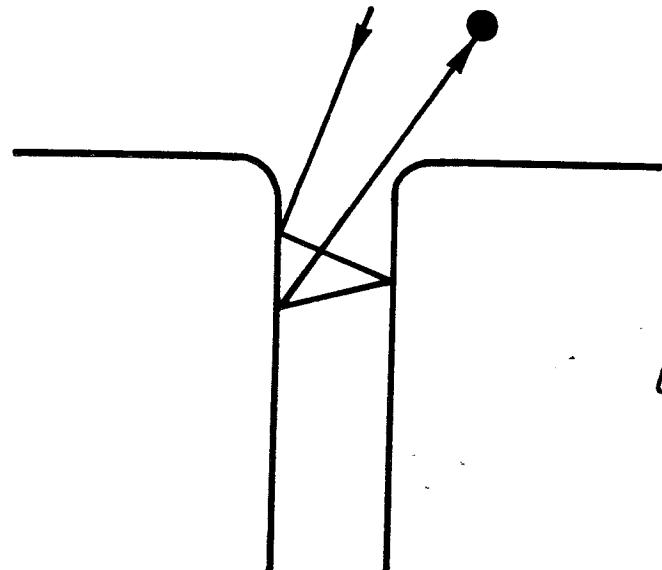
A_V = AREA OF VOID ENTRANCE

D = DIAMETER OF VOIDS

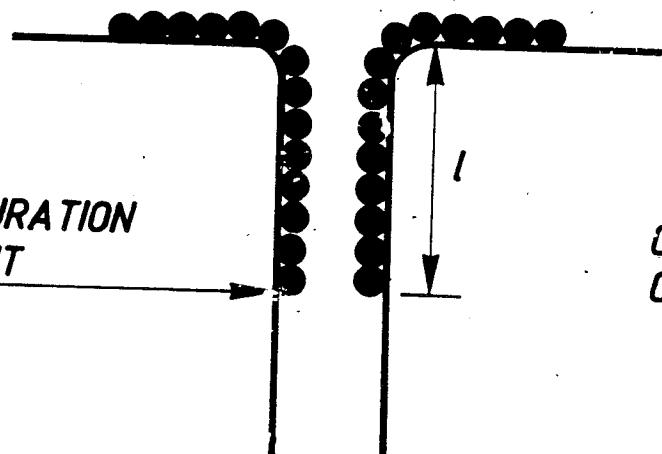
L = LENGTH OF VOIDS

n^2 = NUMBER OF VOIDS/cm²

Q_0 = NUMBER OF ADSORPTION
SITES PER METRE OF
NEG (without VOIDS)



CAPTURE PROBABILITY = α_V



CAPTURE PROBABILITY = $C \times \alpha_V$
 C = CONDUCTANCE TO l

FOR $l \rightarrow \infty$, $\alpha_V \rightarrow 1$
 MONTE CARLO SIMULATION

With this notation the pumping speed of the NEG outer surface may be written as

$$S_f = \alpha_f A_f C \left(1 - \frac{Q}{Q_o (1 - A_v/A)} \right) \quad (3)$$

while S_v , according to the Knudsen formula for molecular flow, may be expressed for N_2 as

$$S_v = \alpha_v n^2 A \frac{12.5 D^3}{\ell + 1.3 D} \quad (4)$$

The gas quantity required to saturate A_f is

$$Q_f = Q_o A_f / A \quad (5)$$

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

$$Q_v = n^2 \pi \ell D Q_o \quad (6)$$

Therefore

$$Q = Q_F + Q_V = (A_F/A + n^2 \pi \ell D) Q_0 \quad (7)$$

$$Q_{\text{sat}} = (A_F/A + n^2 \pi LD) Q_0 \quad (8)$$

and, for $Q \gg Q_0$, combining eq. (7) and eq. (8)

$$\ell \approx L Q_V / Q_{\text{sat}} \quad (9)$$

Finally

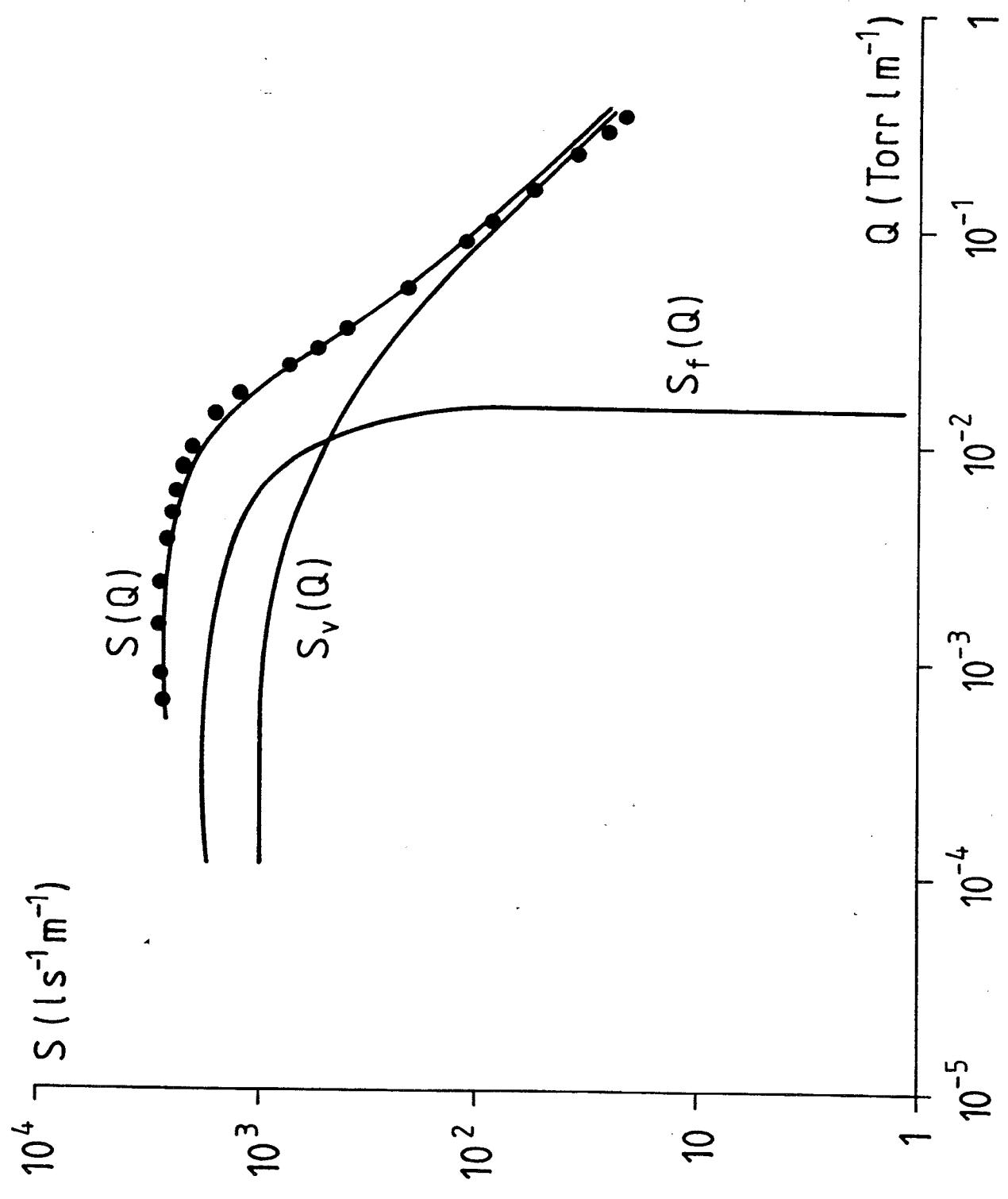
$$S_0 = (\alpha_F A_F + \alpha_V A_V) C \quad (10)$$

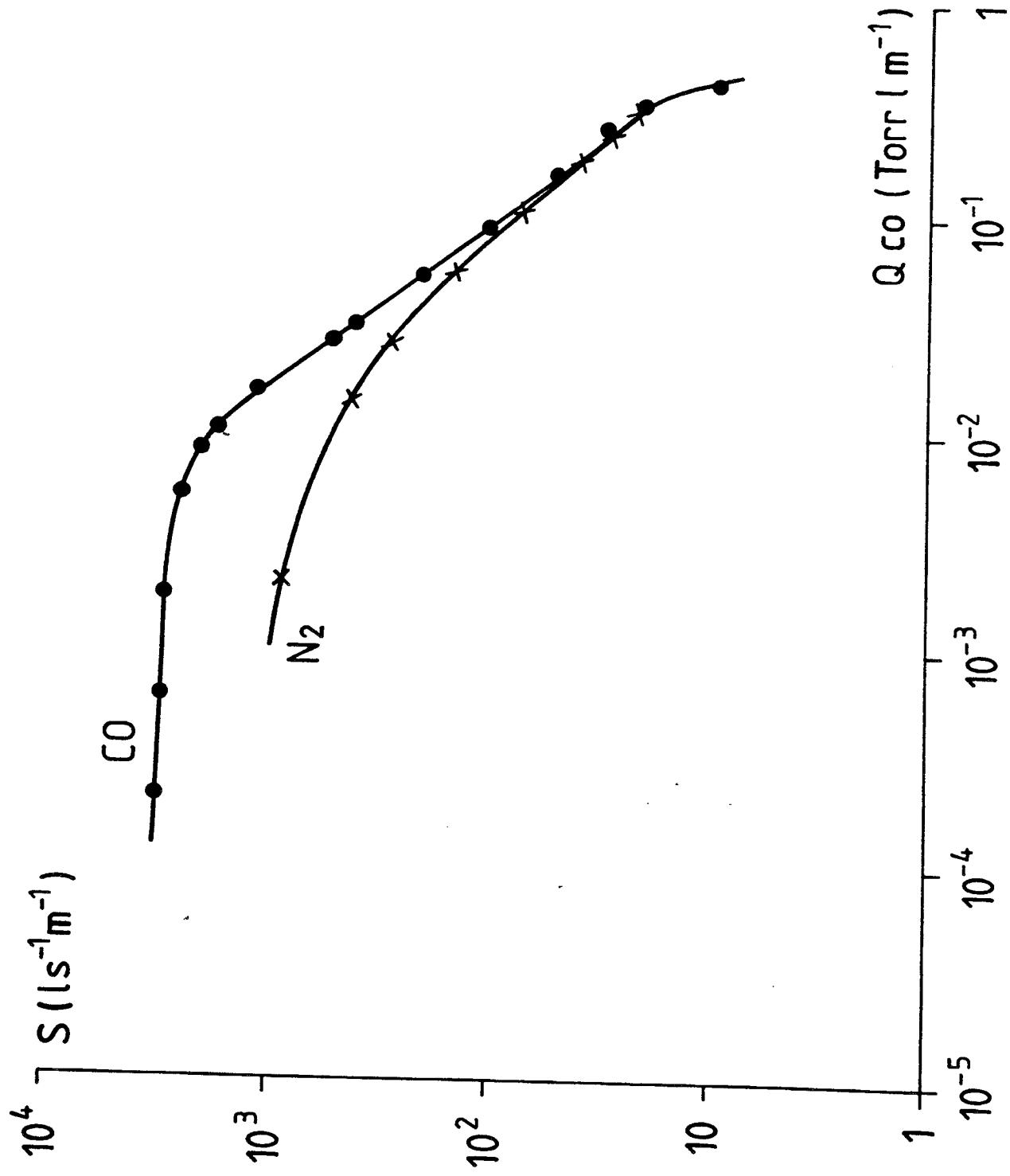
Combining eq. (4) and eq. (6) under the approximation $\ell \gg D$, gives

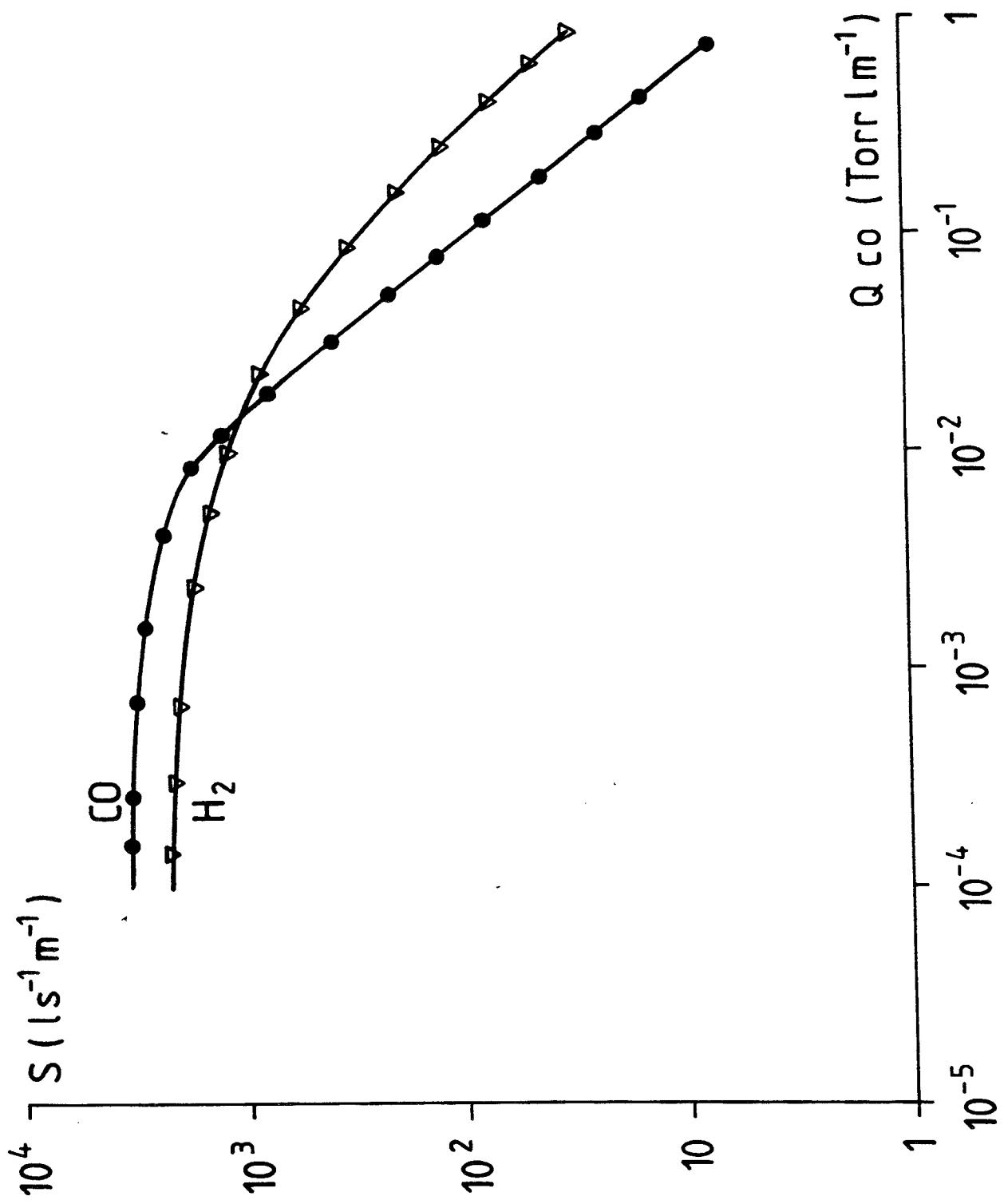
$$S \approx S_V = 3.44 \times 10^4 \alpha_V (A_V/A)^2 Q_0 / Q_V \quad (11)$$

As will be shown later, $D < 1 \mu\text{m}$. On the other hand, $L \approx 100 \mu\text{m}$ and $Q_{\text{sat}} \approx 1 \text{ Torr} \cdot \text{m}^{-1}$ for CO. Since (eq. (9)) $\ell \approx 10 \mu\text{m}$ at $Q \approx 0.1 \text{ Torr} \cdot \text{m}^{-1}$, it may be deduced that above this Q value and for CO, $S \propto Q^{-1}$ as anticipated by eq. (2).

Equation (11) provides the additional important information that, under the known approximation $\ell \ll L$, S is proportional to the square of A./A. This quantity







How a given NEG may be improved?

Increase porosity

$$S \propto (A_v/A)^2$$

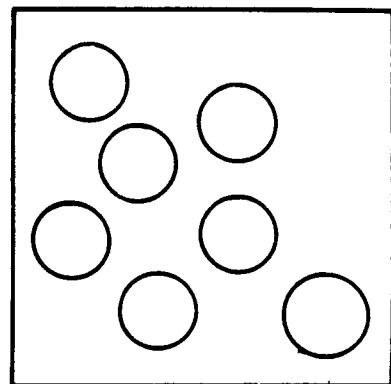
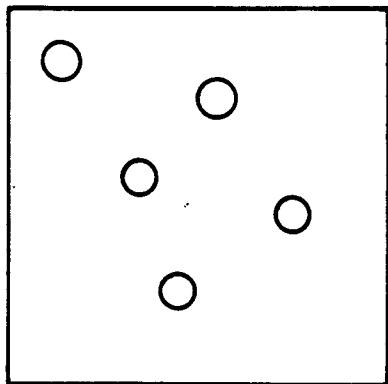
1979 $A_v/A = 0.7$

1981 $A_v/A = 0.11$

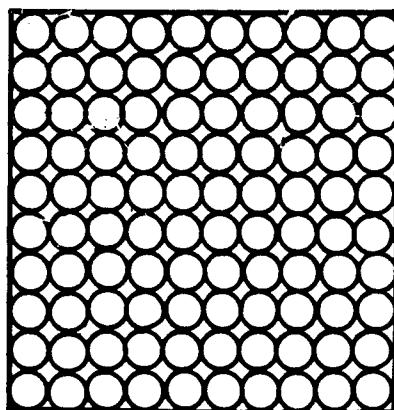
1986 (LEP) $A_v/A = 0.13$

**WHAT IS THE LIMIT TO NEG
IMPROVEMENT ?**

INCREASE n^2 AND D



IDEAL NEG



n^2 VOIDS/cm²

$nD = 1$

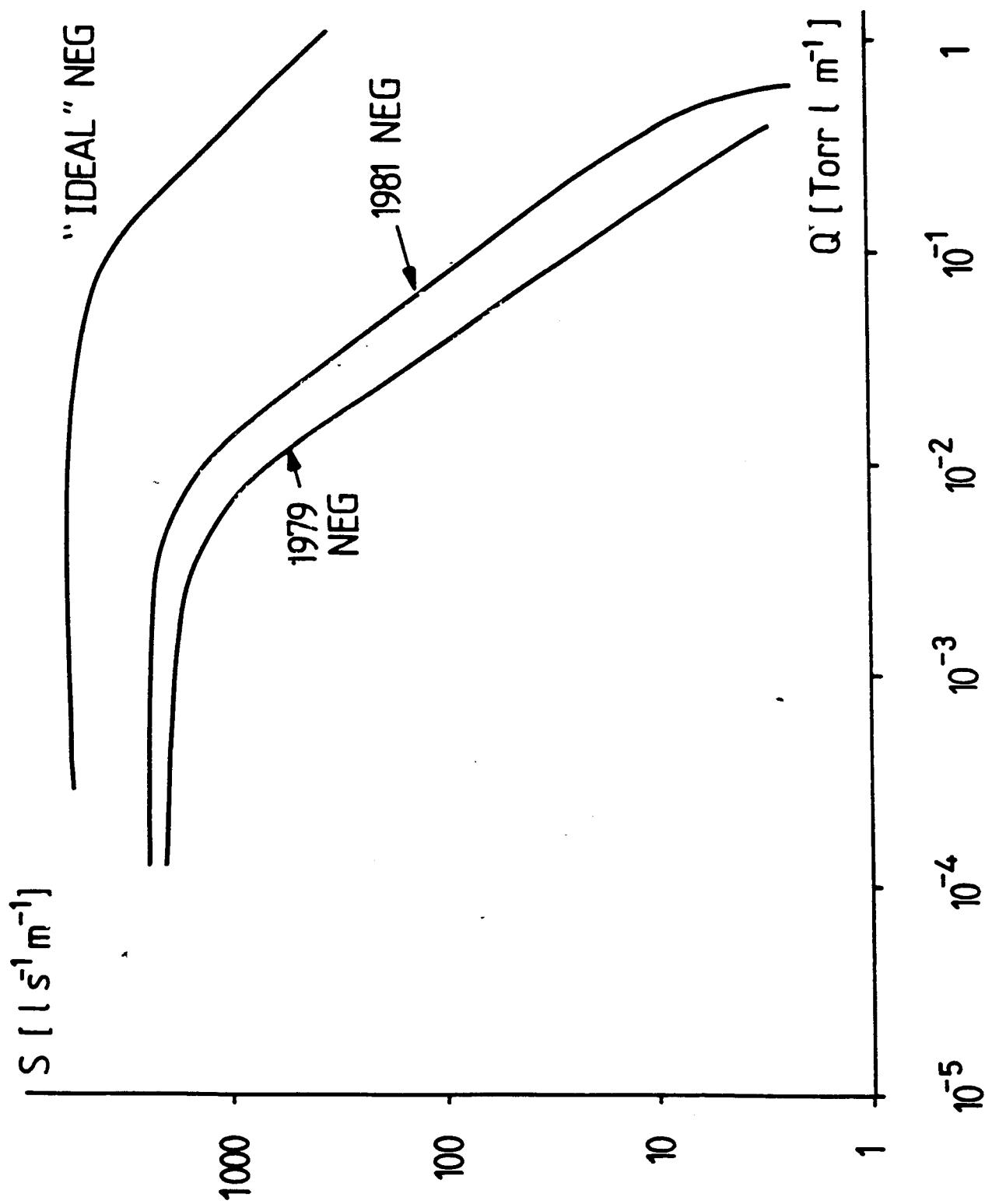


Figure 7

St 101 [8] [9] [10]

Composition	Zr 84%, Al 16% (at. %)
Getter layer thickness	~ 0.1 mm
Activation	750°C for about 30'
Porosity	~ 10%
Substrate	steel or constantan
H ₂ dissociation pressure (pressure p in mbar, H ₂ quantity q in mbar $\ell \text{ g}^{-1}$, T in Kelvin).	$\log(p_{\text{H}_2}) = 4.28 + 2\log(q) - 7000/T$

St 707 [11] [2]

Composition	Zr 70%, V 24.6%, Fe 5.4%
Getter layer thickness	~ 0.1 mm
Activation	400°C for about 1 hour
Porosity	~ 10%
Substrate	steel or constantan
H ₂ dissociation pressure (same units as above).	$\log(p_{\text{H}_2}) = 5.14 + 2\log(q) - 6250/T$

Note that the equilibrium pressure of H₂ over the St 707 (same temperature and H₂ concentration) is about two orders of magnitude higher compared to St 101.

Warning

Due to its low activation temperature, the St 707 may be ignited by spot welding.

A much more favourable situation may be obtained by means of a Zr(70%) - V(24.6%) - Fe(5.4%) NEG (St 707 SAES Getters) which requires lower activation temperature (300°C - 400°C) and consequently may be passively activated during the bake-out.



Electrical insulation is not needed



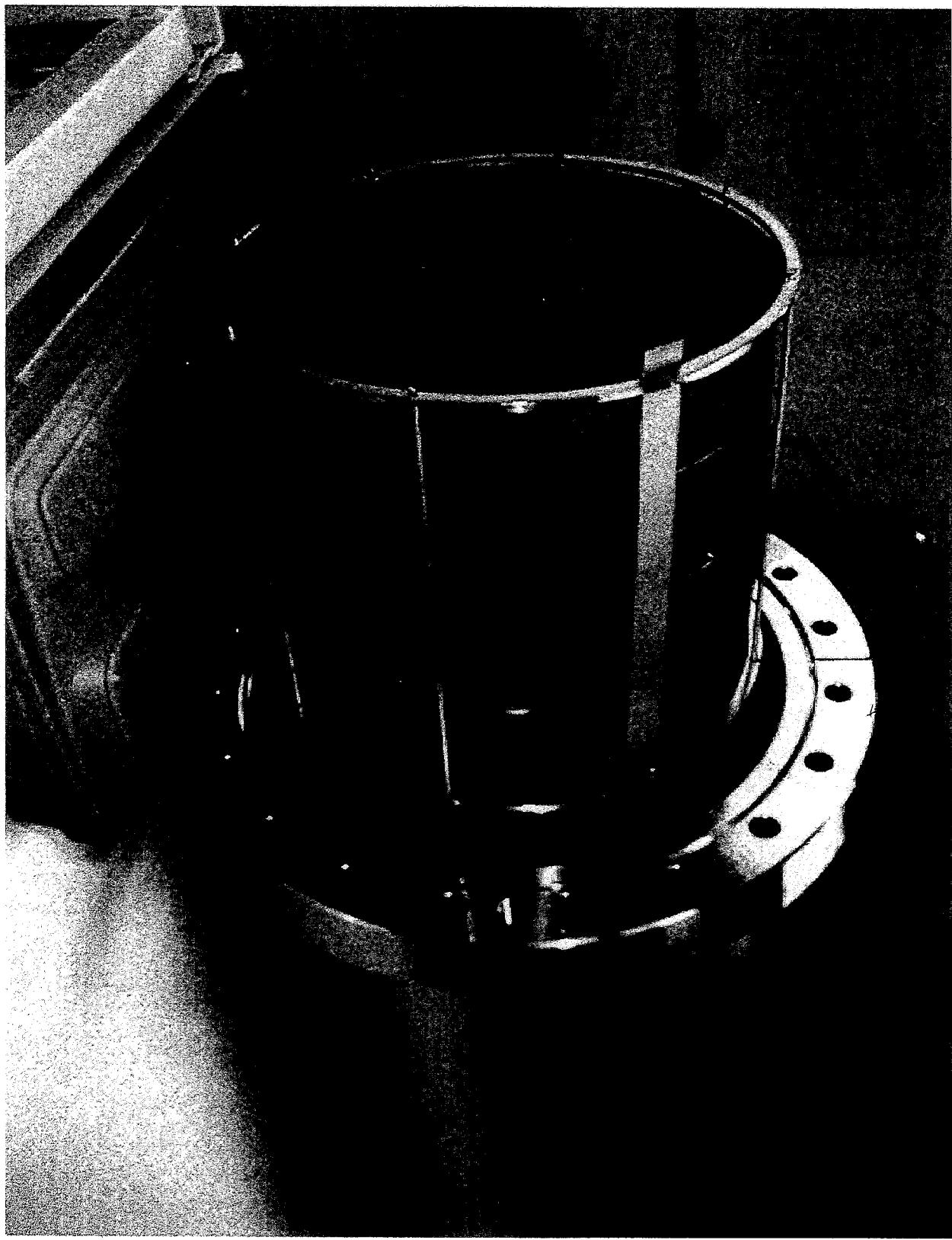
NEG strip may be closely packed in contact with the vacuum chamber wall

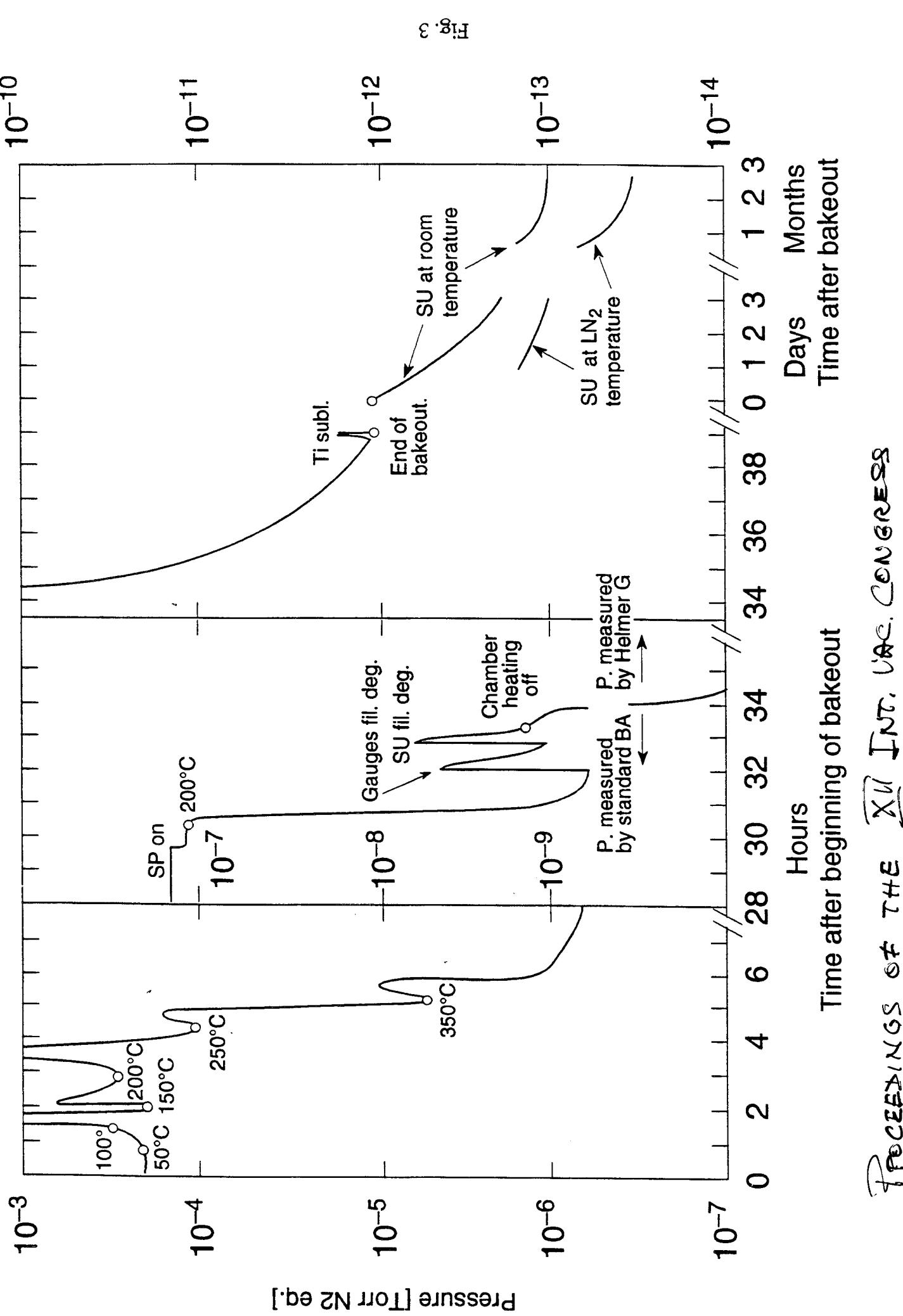


The ratio of vacuum system to NEG surface areas could be as low as 0.5, i.e. about 30 times lower than in the case of LEP

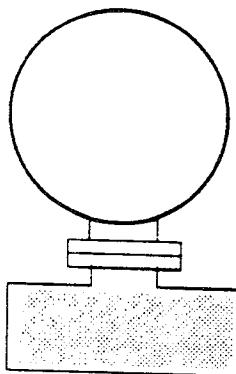


Larger pumping speed → lower pressure

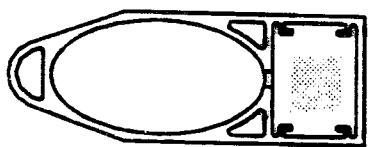




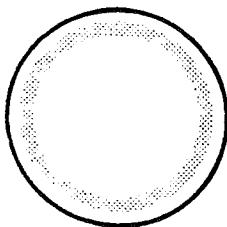
Vacuum system configuration



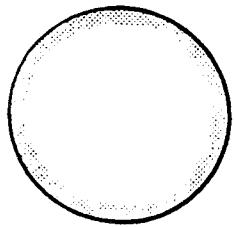
appendage pump



inserted "linear" pump



inserted "total" pump



surface pump/diffusion barrier

4. Thin film getter coatings

Thin film NEG coatings represent the last step of a process during which the pump became progressively closer to the vacuum chamber walls. The getter thin film coating actually transforms the vacuum chamber from a gas source into a pump.

Many metal coatings have been studied at CERN during the last 3 years, namely Ti, Zr, Hf, Nb, V and some of their binary and ternary alloys [17] [18]. The coating is carried out by sputtering.

The main goal was to reduce the activation temperature so as to allow activation also when using aluminium vacuum chambers, which cannot be baked at temperatures higher than about 200°C. This goal has been achieved with a TiZrV alloy [19], which would be highly pyrophoric when used as a powder, but does not present this risk in the form of a thin film, thanks to the thermal stabilisation provided by the much thicker substrate. The main results achieved using this coating are shown in Fig. 6 and 7.

The study is still in progress in view of an application of this technique to the Large Hadron Collider (LHC) which will be built at CERN in the very near future.

Goal

To sputter-coat the inner walls of a vacuum chamber with a thin film of a low activation temperature NEG, which is activated during bakeout

therefore

$T_{act} \leq 400^\circ\text{C}$ for stainless steel chambers
 $\leq 200^\circ\text{C}$ for Cu and Al chambers

in any case

$T_{act} > 100-150^\circ\text{C}$

to guarantee stability in air at room temperature

and

avoid water vapour absorption during bakeout

Benefits

The NEG coating should

- trap the gas coming from the underlying surface
- after activation, provide a clean surface, resulting in a pumping action and reduced degassing (both thermal and ion/radiation/electron induced)

i.e.

transform the vacuum chamber from a gas source to a pump which does not need space, electric powering, feedthroughs...

2. Material selection

"Vacuum" selection criteria

- I) Chemical affinity for reactive gases
(H₂, CO, CO₂, O₂, N₂...)
- II) For H₂
 - Very high diffusion coefficient
 - Large absorption capacity
 - Low dissociation pressure
- III) For O₂
 - High diffusion coefficient
 - Large solubility limit
- IV) Stability in air at ambient temperature
 - Requirements III and IV are contradictory:
→ compromise 150°C ≤ T_{act} ≤ 200°C
 - Most restrictive requirement is the O₂ solubility

3. Production

Sputtering ideal, because

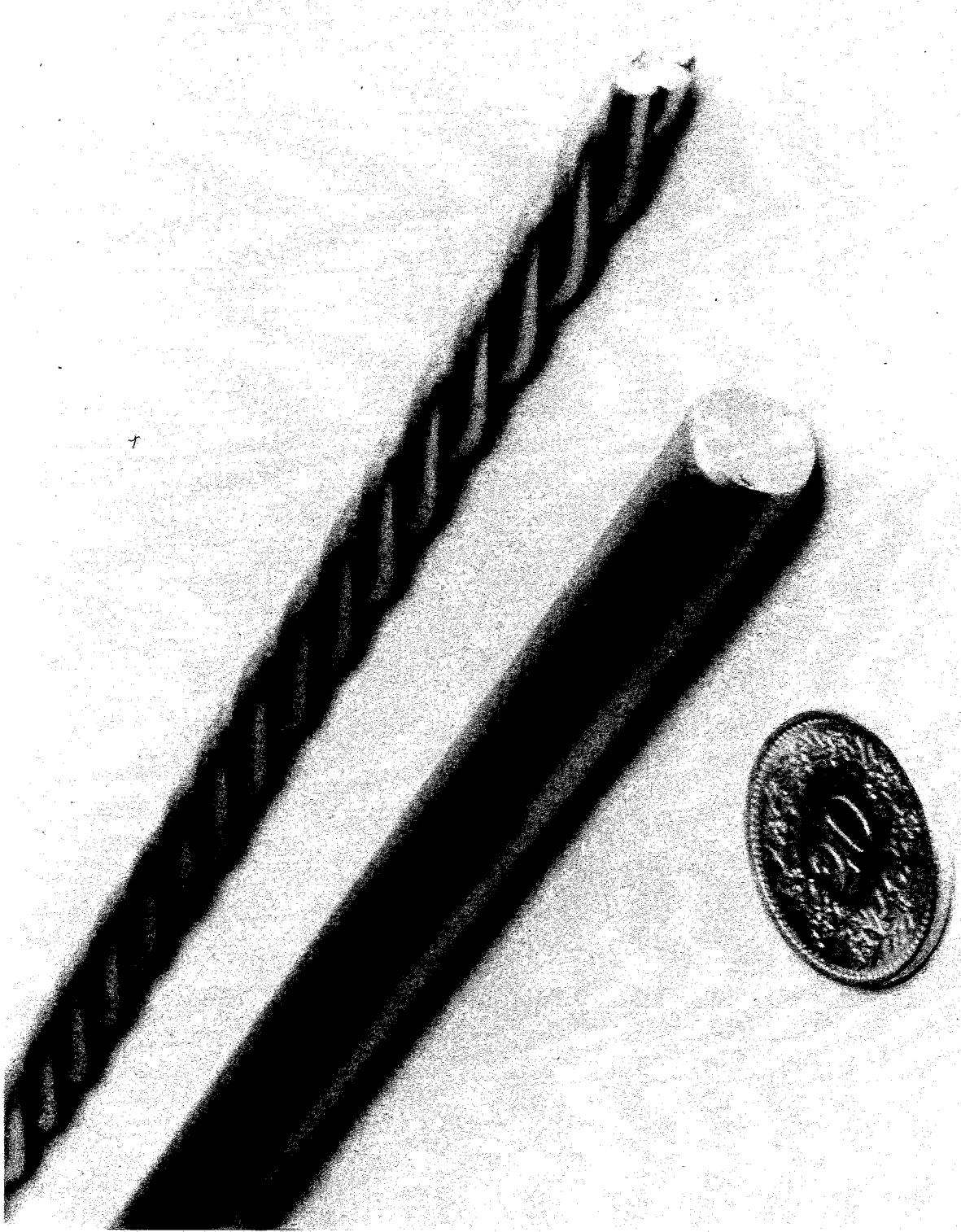
- Simple, suitable for a wide range of materials
- Keeps stoichiometry of alloys
- Suitable for distributed coating
- Allows co-sputtering from composite cathodes

Composite cathodes are very interesting, because

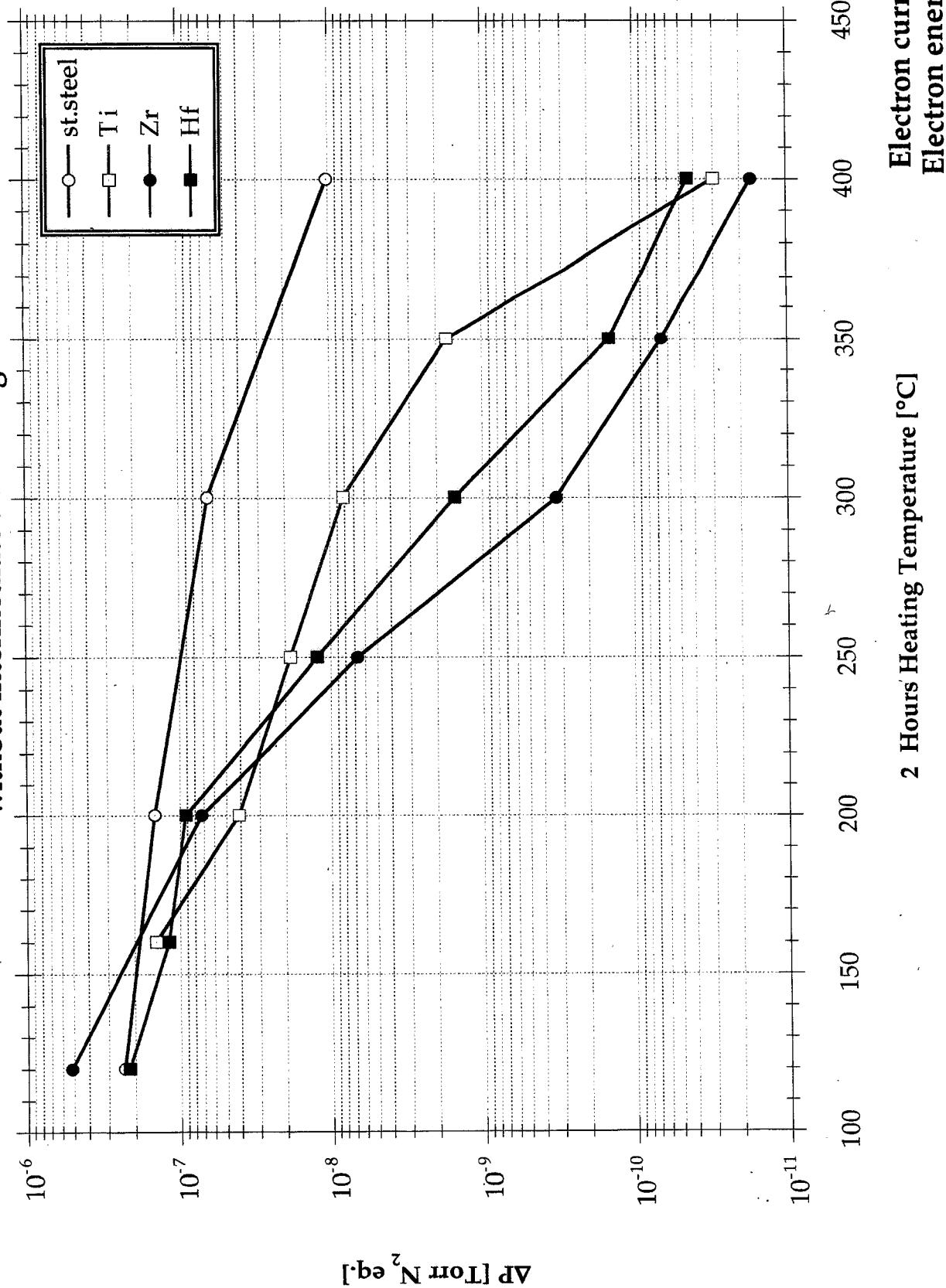
- Allow the production of compounds/alloys starting from easily available pure metals
- Remove the problem of cathode pyrophoricity
- Allow the production of materials non existing in nature (metastable alloys)

Important

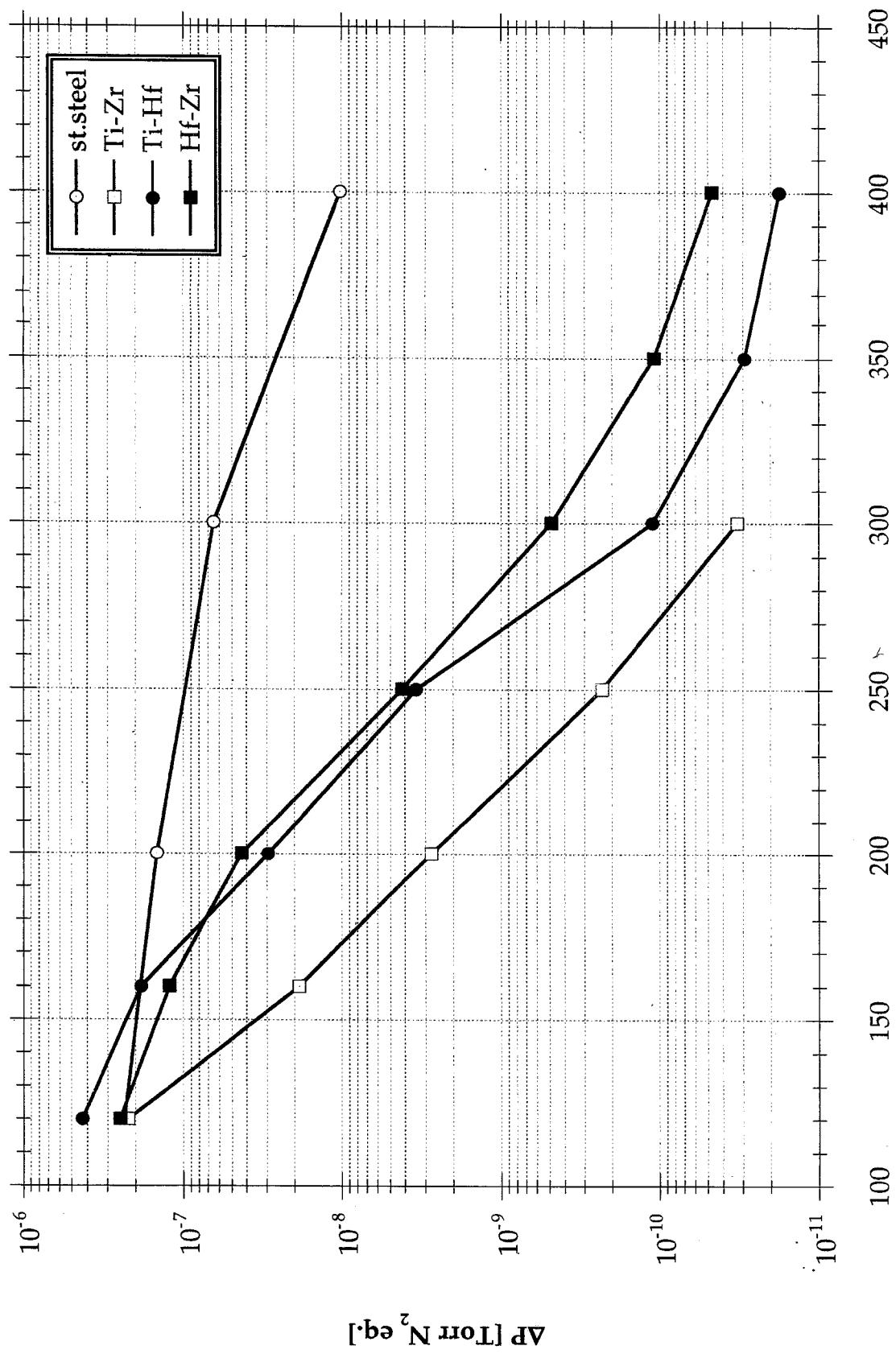
Materials which are pyrophoric as bulk or powder are stable as coatings (thermal stabilization by the substrate)



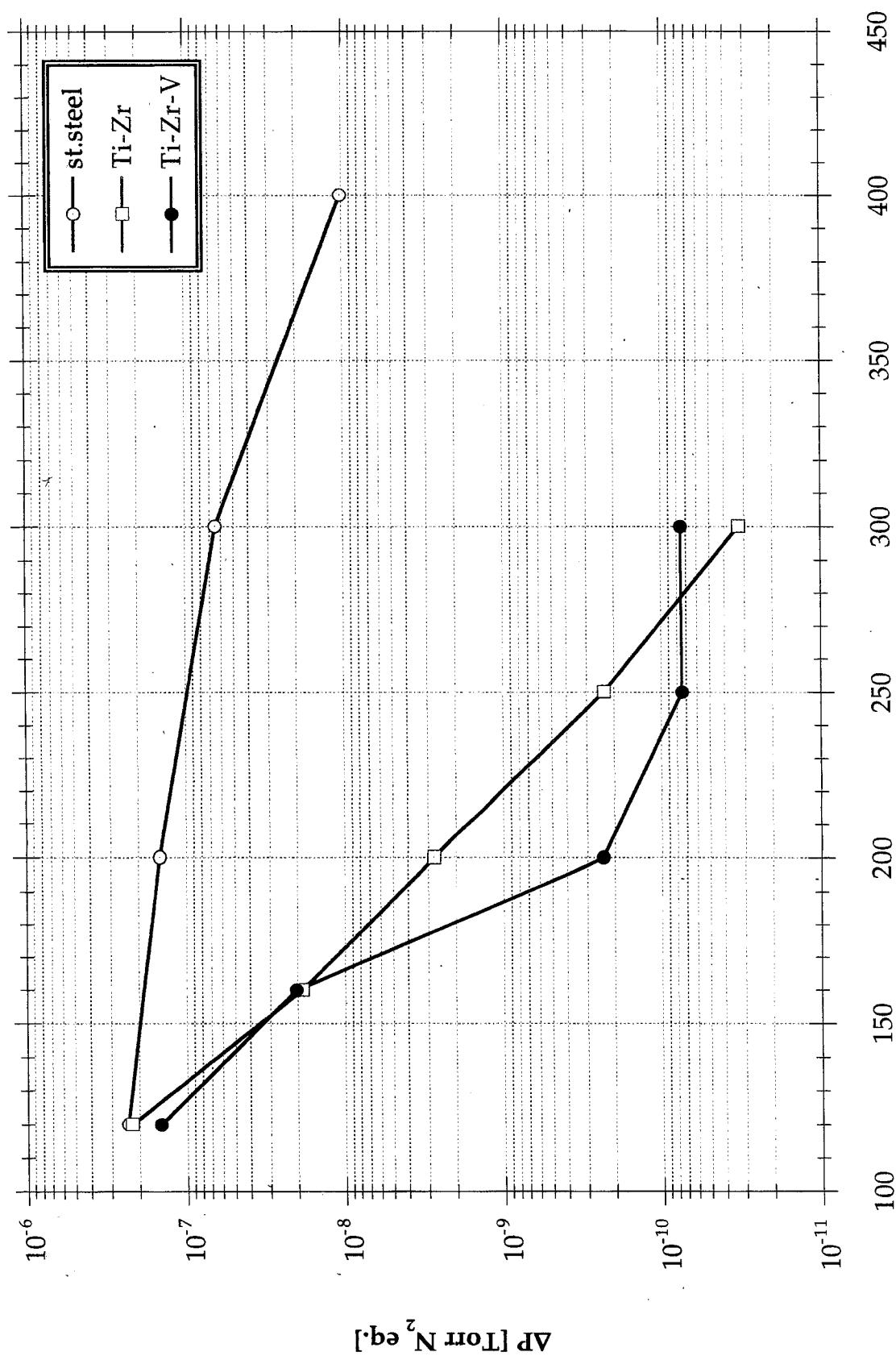
**Measured at room temperature
after heating at the indicated temperature (2h)
without intermediate air venting**

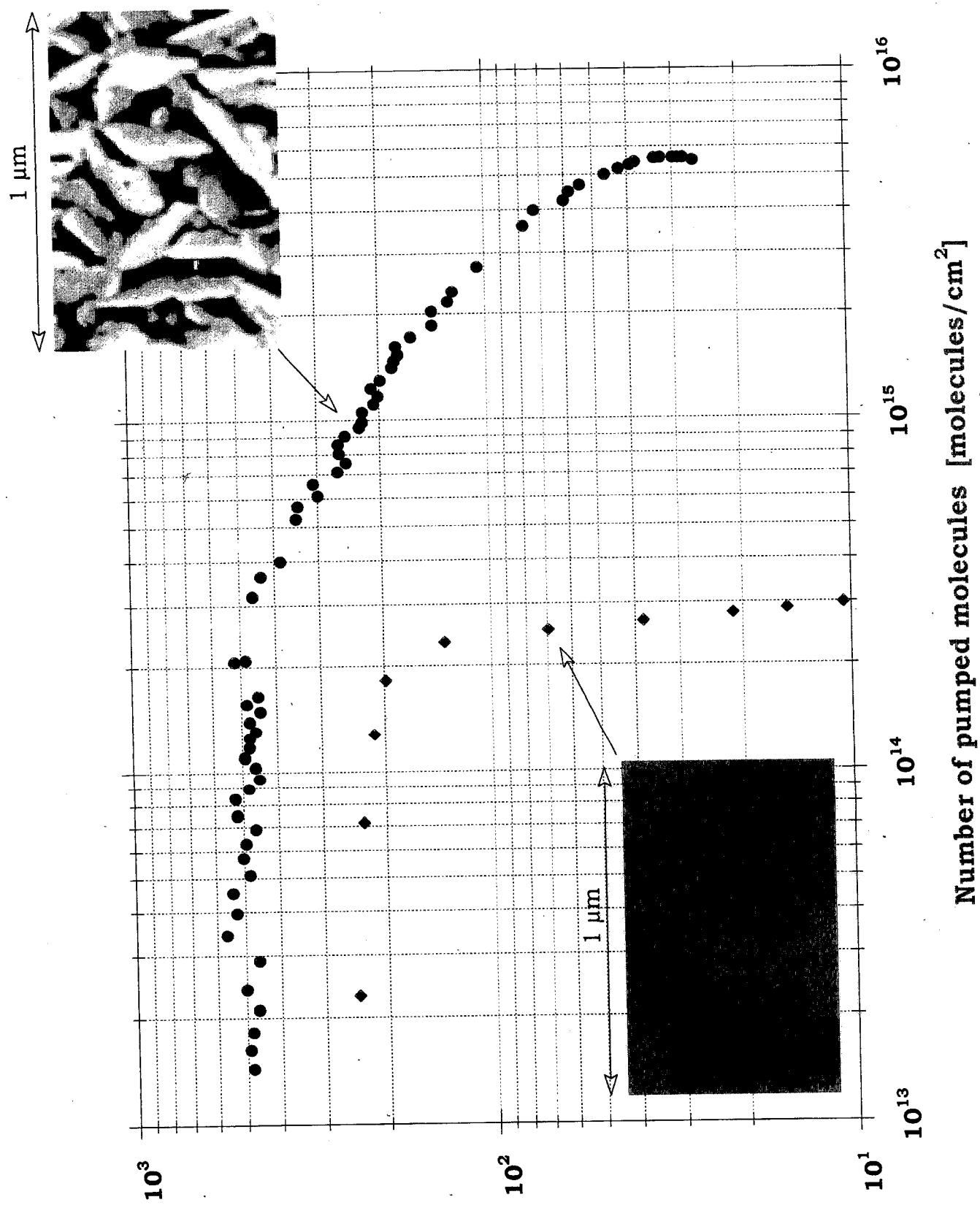


2 Hours Heating Temperature [°C]

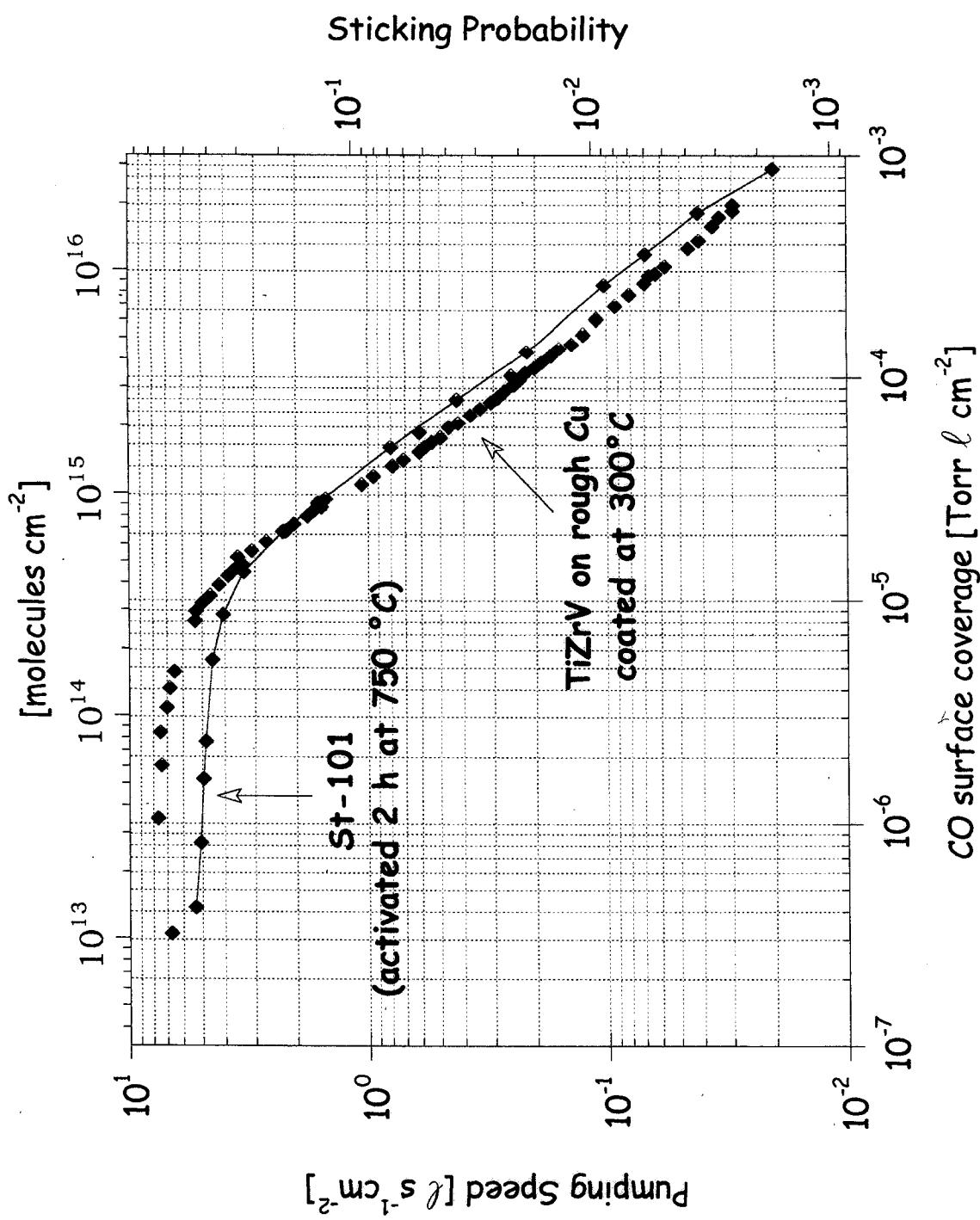


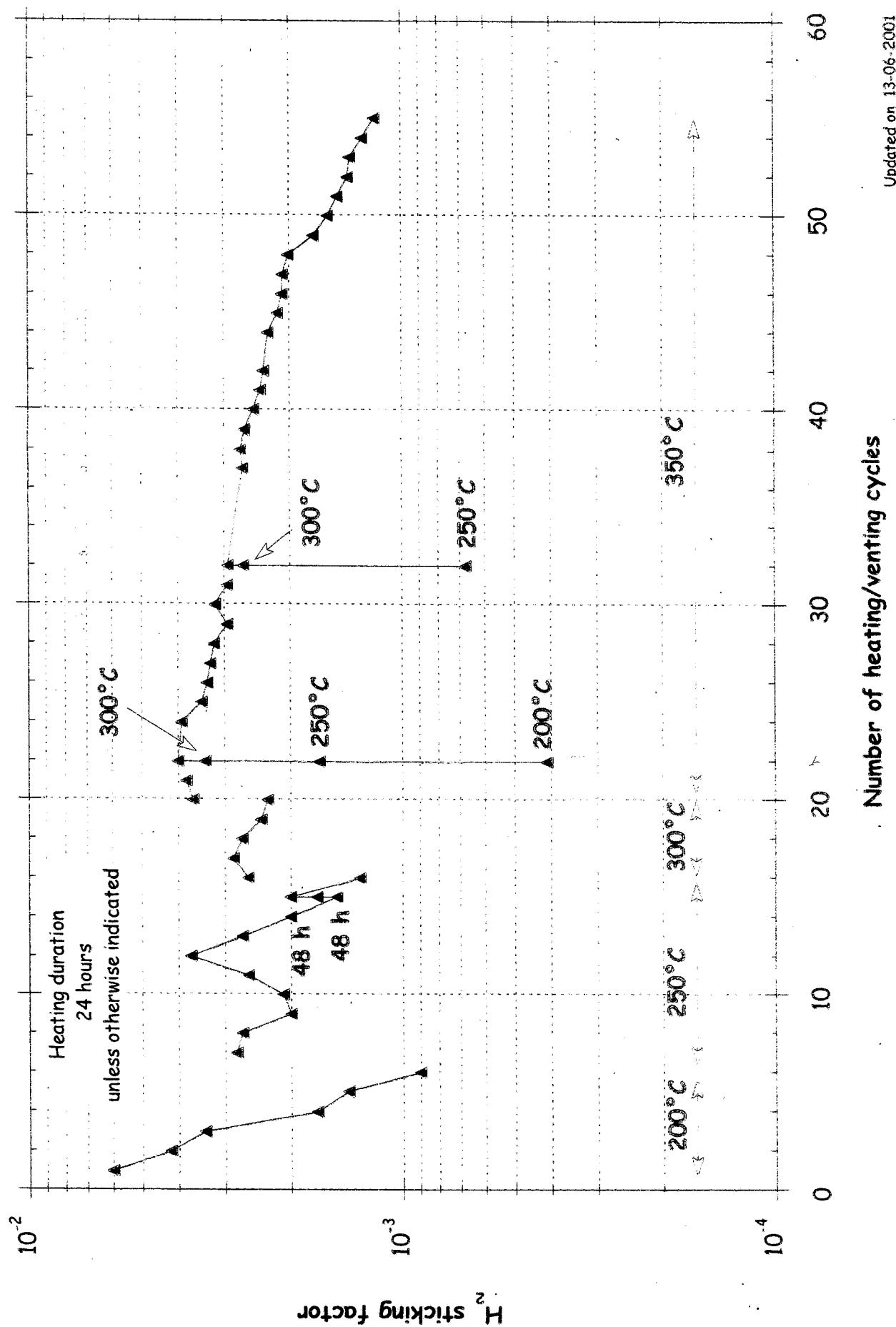
2 Hours Heating Temperature [°C]





Pumping Speed at the entrance of sample [g/s] (sample dimension $D=10 \text{ cm}$, $L=50 \text{ cm}$)

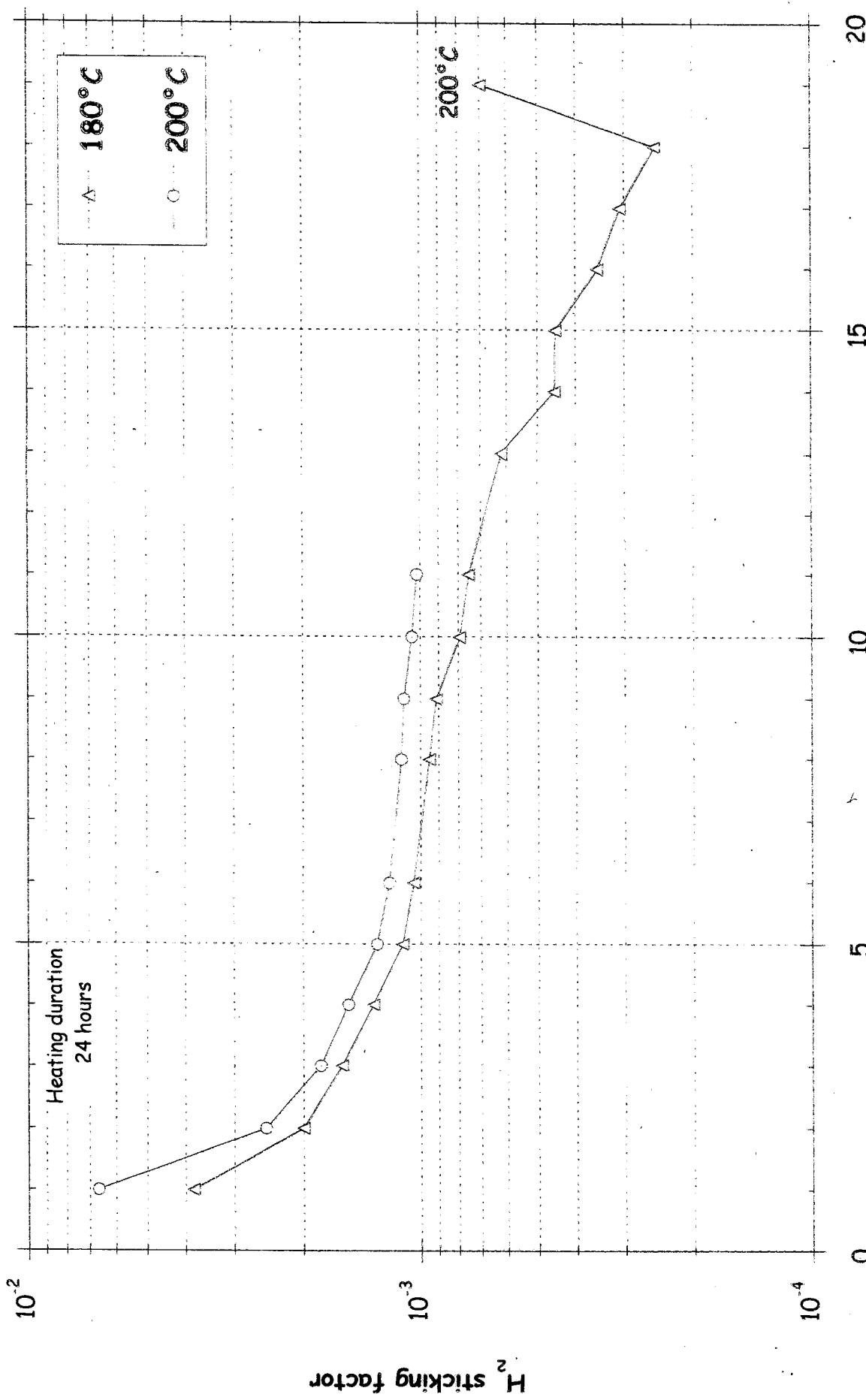




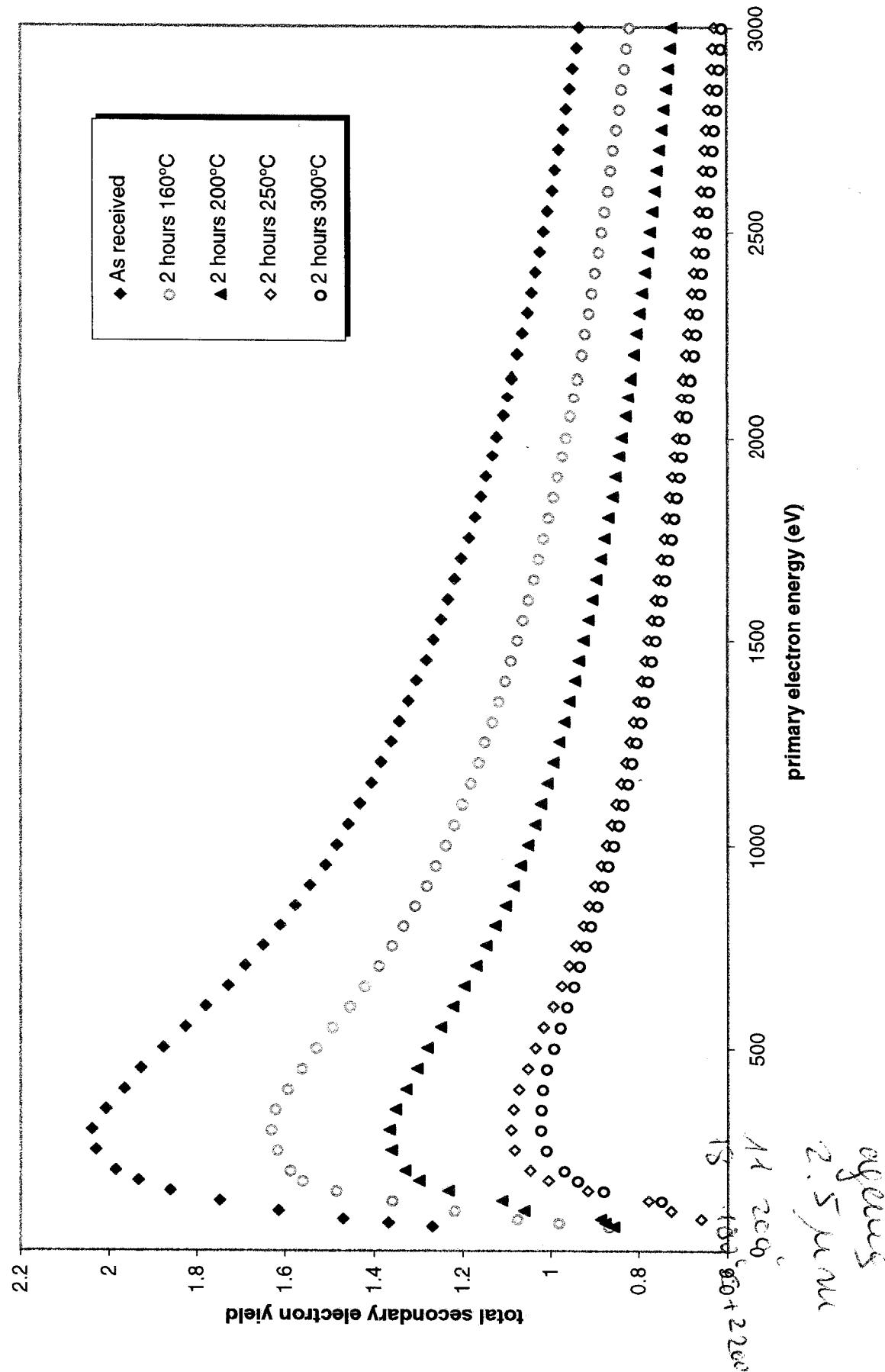
Updated on 13-06-2001

Number of heating/venting cycles

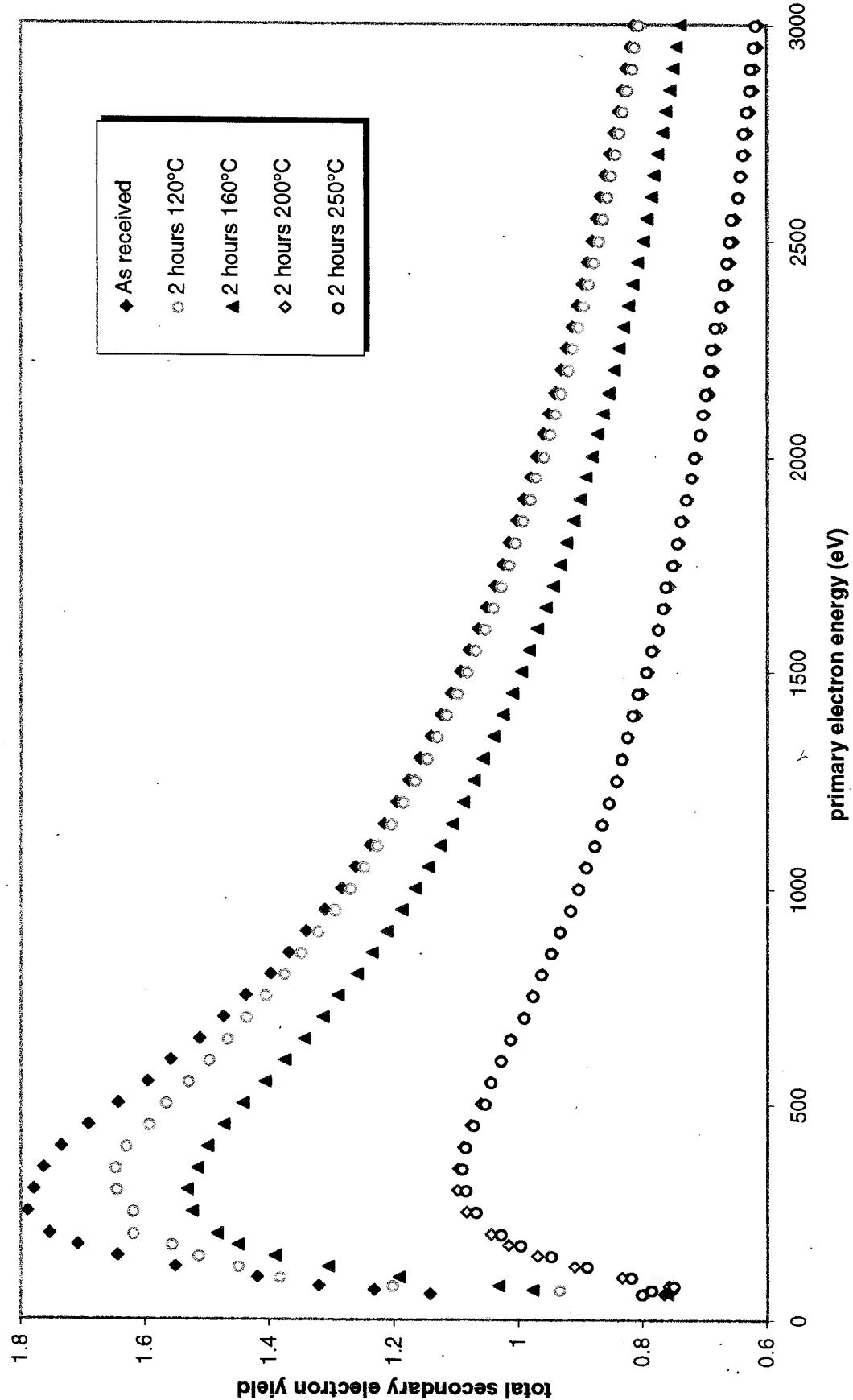
Updated on 14-06-2001



SEY of NEG TiZr on Cu, as received and after 160°C, 200°C, 250°C and 300°C activation



SEY of NEG TiZrV on 316LN, as received and after 120°C, 160°C, 200°C, and 250°C activation



TiZrV to 250C

Performance

1. Pumping speed

For H₂, average 0.35, max 1 $\text{ls}^{-1} \text{cm}^{-2}$,

For CO, average 6, max 10 $\text{ls}^{-1} \text{cm}^{-2}$.

2. Ultimate pressure

Not measurable (lower than 10⁻¹³ Torr)

provided that rare gases and methane are removed by a pump of a different type.

3. Surface capacity

Up to 10¹⁶ molecules cm⁻² for CO, same as that of available getters based on powder technology.

4. Ageing

Up to 50 venting cycles possible with a marginal performance loss.

5. Secondary electron yield

Down to 1.1 (peak value).

6. Argon degassing

Lower than 10⁻¹⁷ Torr $\text{ls}^{-1} \text{cm}^{-2}$

Conclusions

Non-Evaporable Getter thin film coatings present many attractive features, of which the following are worth mentioning:

- Low activation Temperature (180 °C)
- Large surface pumping, which may be distributed linearly to counteract conductance limitations
- H₂ outgassing of the underlying material irrelevant
- Major reduction of degassing induced by surface bombardment (2 orders of magnitude)
- Low secondary electron yield (peak value not higher than 1.1)

The solution is robust

- Fast pump-down, activation in poor vacuum is feasible (10^{-5} Torr)
- Partial, non simultaneous activation is possible
- Only small additional pumps are required

The two main inconveniences of NEG coatings are:

- The **limited life**
- The need of **heating** for activation

Materials which do not produce a surface passivation layer when exposed to air would not present these inconveniences.

Do they exist?

Obviously, these materials would present the drawbacks of :

- selective pumping
- low binding energies for the reacting gases

Materials with these properties exist within the family of CATALYSTS.

Palladium thin film coatings on different substrates were extensively studied.

Exploratory measurements were carried out also on platinum coatings.

CATALYSTS

From Greek

Kατὰ	λύω
Down	Break

“Subsistances are able to awake affinities which are asleep at this temperature by their mere presence...”

J.J. Berzelius, 1836

The usually accepted definition of a *catalyst* is that it is *a substance that increases the rate at which a chemical system approaches equilibrium, without being consumed in the process.*

G.C. Bond
Heterogeneous catalysis
Clarendon Press – Oxford, 1987

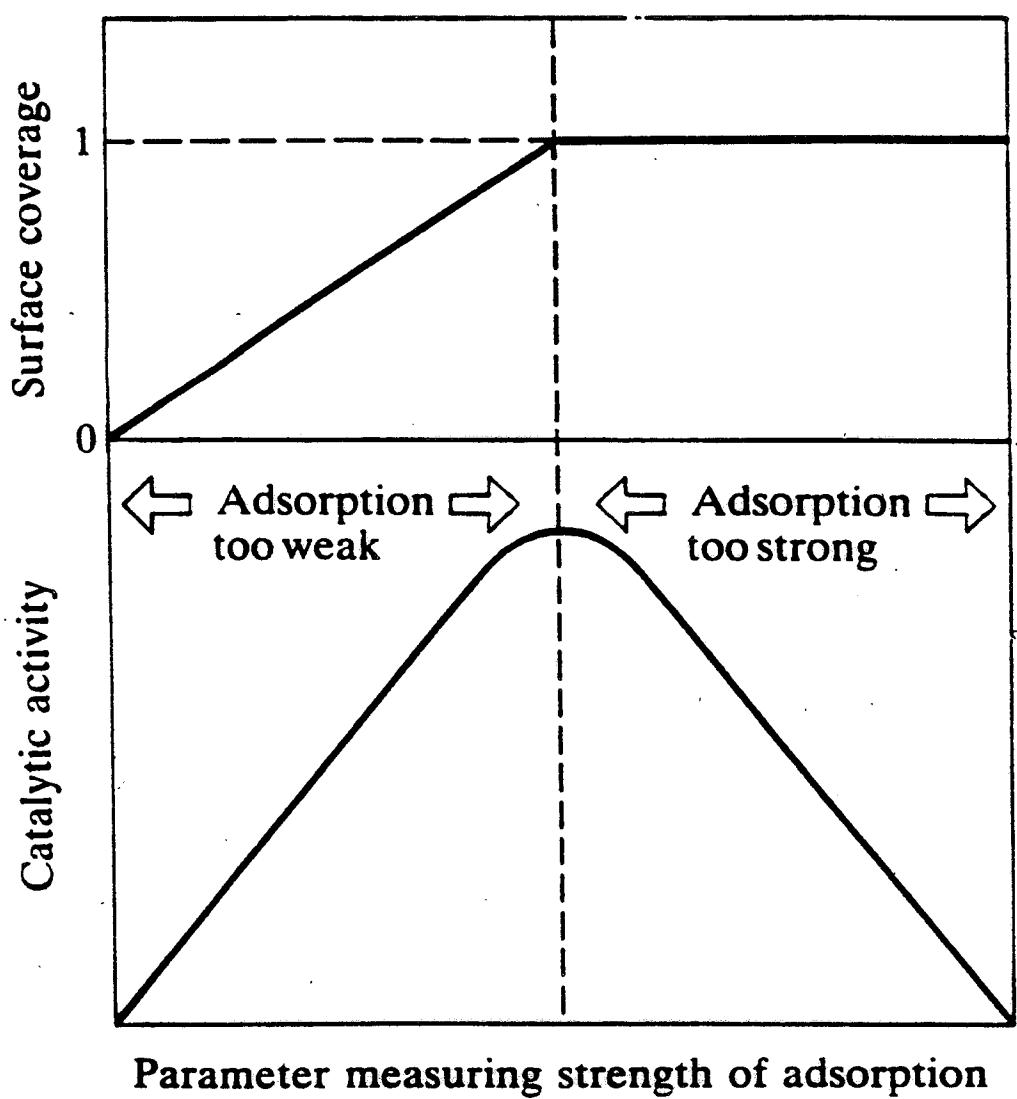


FIG. 6.1. The volcano curve: dependence of catalytic activity upon strength of reactant adsorption (lower part) and the corresponding variation in surface coverage (upper part).

