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ION INDUCED DESORPTION COEFFICIENTS FOR  
TITANIUM ALLOY, PURE ALUMINIUM AND STAINLESS STEEL

by

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CERN LIBRARIES, GENEVA



CM-P00064841

Geneva, 1st March 1976

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## 1. INTRODUCTION

In proton storage rings an average pressure  $< 1 \times 10^{-11}$  torr is necessary to minimize background in the experimental regions and beam decay rate due to interaction of the protons with the residual gas<sup>1)</sup>. However, ionization of the residual gas by the proton beam and subsequent bombardment of the vacuum chamber walls by ions with energies  $\approx 2$  keV result in release of adsorbed gas and large pressure increases which are detrimental to the running of the machine.

To investigate the stability, under ion bombardment, of possible vacuum chamber materials, an apparatus was constructed which enabled us to identify and quantify the species desorbed from these materials by 2 keV ions by measuring the increase in pressure  $\Delta P$  for a given pumping speed  $S$ , the product  $S\Delta P$  being the number of molecules per second desorbed by the incident ions.

## 2. THEORY

### 2.1 The laboratory desorption coefficient $\eta_L$

The desorption coefficient  $\eta_L$  is defined as

$$\eta_L = \frac{\Delta Q}{I/e} \text{ mol. ion}^{-1}$$

where  $\Delta Q$  is the number of molecules desorbed  
 $I$  is the bombarding ion current in amps  
 $e$  is the electronic charge.

For a gas  $g$ , for which the pumping speed of the system is  $S_g (\text{ls}^{-1})$  and the corresponding rise in absolute pressure is  $\Delta P_g (\text{Abs})$  the expression for  $\eta_L$  may be written

$$\eta_L = \frac{5.23}{I} \sum_g [S_g \Delta P_g (\text{Abs})]$$

where the summation is taken over all gases desorbed and the factor 5.23 takes account of the conversion from molecules  $\text{s}^{-1}$  ( $\Delta Q$ ) to torr  $\text{ls}^{-1}$  ( $S_g \Delta P_g (\text{Abs})$ ) and also  $e$ .

If we write

$$\Delta P_g(\text{Abs}) = \Delta P_g(\text{N}_2 \text{ equiv}) \times K_g$$

where  $K_g$  is the relative calibration factor for gas  $g$  and

$$\Delta P_g(\text{N}_2 \text{ equiv}) = F_g \times \Delta P_{\text{total}}(\text{N}_2 \text{ equiv})$$

where  $\Delta P_{\text{total}}(\text{N}_2 \text{ equiv})$  is the total change in pressure read on the vacuum gauge (in  $\text{N}_2$  equivalent) on desorption and  $\Delta P_g(\text{N}_2 \text{ equiv})$  is the partial change in pressure of gas  $g$  (in  $\text{N}_2$  equivalent) and the fraction of  $\Delta P_{\text{total}}(\text{N}_2 \text{ equiv})$  due to desorption of gas  $g$  is  $F_g$ , obviously

$$\sum_g F_g = 1 \quad \text{and} \quad 0 \leq F_g \leq 1$$

the final expression for  $\eta_L$  is therefore

$$\eta_L = \frac{5.23}{I} \Delta P_{\text{total}}(\text{N}_2 \text{ equiv}) \sum_g S_g K_g F_g \quad (1)$$

which can be written as a sum of partial  $\eta$ 's =  $\eta_g$

$$\eta_L = \sum_g \eta_g \quad \text{where} \quad \eta_g = \frac{5.23}{I} \Delta P_{\text{total}}(\text{N}_2 \text{ equiv}) S_g K_g F_g \quad (2)$$

Thus for a reliable calculation of  $\eta_L$  when several desorbed species are involved, the pumping speed of the system for each species  $S_g$  must be known, a total pressure gauge calibrated for each species  $g$  is required ( $K_g$ ) and also a calibrated residual gas analyser for identification of the desorbed species and the calculation of  $F_g$ .

For an estimate of the  $\Delta P_{\text{total}}(\text{N}_2 \text{ equiv})$  let us assume that only  $\text{N}_2$  is desorbed ( $F_g = 1$  and  $K_g = 1$ ), the pumping speed of the system for  $\text{N}_2$  is  $35 \text{ l s}^{-1}$ , the ion current is  $4 \times 10^{-8} \text{ A}$  and the  $\eta_L$  for the sample is  $1 \text{ mol. ion}^{-1}$ .

From equation (1) the  $\Delta P_{\text{total}}$  ( $N_2$  equiv) is  $\approx 2.2 \times 10^{-10}$  torr. Thus the background pressure in the measuring chamber must be sufficiently low to observe changes in pressure in the  $10^{-10}$  torr range. The lowest detectable  $\eta_L$  is of the order of  $0.01 \text{ mol. ion}^{-1}$ .

In all diagrams in this publication the desorption coefficient quoted is  $\eta_g$ .

## 2.2 The machine desorption coefficient $\eta_M$ related to $\eta_L$

We consider the desorption process to consist of three separate mechanisms :

- (a) the creation of ions from the gas phase (in a storage ring) or introduction via an external source as in the laboratory.
- (b) The desorption of gas molecules from the surface by the incident ion.

This we define as  $\eta_{\text{true}}$  and is different for different ion species. Only those molecules which remain long enough in the gas phase to be detected are considered to be contributing to  $\eta_{\text{true}}$  i.e. sputtered metal atoms are neglected ( $\eta_{\text{true}} \geq 0$ ).

- (c) The probability of neutralisation and re-emission of the incident ion into the gas phase.

This probability we define to be  $C$  ( $0 \leq C \leq 1$ ). This quantity  $C$  depends on the ion species, the nature of the target and also on bombardment time.

A possible fourth mechanism exists - namely the pumping effect of trapped neutralised incident ions and also that of sputtered target material (Fe, Ti). This mechanism we have neglected.

In addition it must be remembered that all these mechanisms are functions of energy. Our  $\eta_{\text{measured}}$  is therefore given by

$$\eta_{\text{measured}} = (b) + (c) - (a)$$

It is interesting to consider the limiting values (after a very long bombardment time) of  $\eta_{\text{measured}}$ . When the surface bombarded has no desorbable gas left,  $\eta_{\text{true}} = 0$ .

The behaviour of C is more complicated. When ions are implanted in surfaces they are neutralised and some diffuse back to the surface. In the limit, i.e. after a long bombardment time, the surface layers become saturated and one atom per incident ion is re-emitted into the gas phase. With the low ion currents bombarding both the machine vacuum chamber and the samples in the laboratory, this limit will probably never be reached.

To relate  $\eta_M$  to  $\eta_L$  we consider a two residual gas system such as exists in the ISR with a fraction F of  $\text{H}_2$  and 1-F of CO ( $0 \leq F \leq 1$ ). It is assumed that all measurements are made with a residual gas analyser and that only  $\text{H}_2$  and CO are present on the surface.

If, for 26 GeV protons, the ionisation cross-sections for  $\text{H}_2$  and CO are  $\sigma_{\text{H}_2}$  and  $\sigma_{\text{CO}}$  respectively, then the probability that a bombarding ion is  $\text{H}_2^+$  is

$$\frac{F \sigma_{\text{H}_2}}{\sigma_{\text{CO}} - F(\sigma_{\text{CO}} - \sigma_{\text{H}_2})}$$

and that it is  $\text{CO}^+$  is

$$\frac{(1 - F) \sigma_{\text{CO}}}{\sigma_{\text{CO}} - F(\sigma_{\text{CO}} - \sigma_{\text{H}_2})}$$

Since  $\frac{\sigma_{\text{H}_2}}{\sigma_{\text{CO}}} = \frac{1}{5}$  these expressions reduce to

$$\frac{F}{5 - 4F} \quad \text{and} \quad \frac{(1 - F)5}{5 - 4F}$$

We consider first what  $\eta$  is measured in the ISR when looking only at the changes in the  $H_2$  peak of a residual gas analyser. Thus, in the first stage (a) the probability that a hydrogen molecule is ionised and hence removed from the gas phase is  $\frac{F}{5 - 4F}$ .

The probability that this molecule is returned to the gas phase by neutralisation and re-emission of the ion (stage (c)), is given by

$$\frac{F}{5 - 4F} C_{H_2}.$$

In the second stage (b) the surface is bombarded by both  $H_2^+$  and  $CO^+$  and since we are only looking at desorption of  $H_2$ , the  $\eta$ 's involved are  $\eta(H_2^+, H_2)$  and  $\eta(CO^+, H_2)$  where  $\eta(H_2^+, H_2)$  is the desorption coefficient for  $H_2$  molecules desorbed by  $H_2^+$  ions with a similar definition for  $\eta(CO^+, H_2)$ . The  $\eta_{true}$  is then the appropriate weighted sum of  $\eta(H_2^+, H_2)$  and  $\eta(CO^+, H_2)$ , namely

$$\frac{F}{5 - 4F} \eta(H_2^+, H_2) + \frac{(1 - F)5}{5 - 4F} \eta(CO^+, H_2)$$

The resultant measured  $\eta$  for  $H_2$  desorption in the ISR  $\eta_M(H_2)$  is therefore given by (b) + (c) - (a) and may be written as

$$\eta_M(H_2) = \frac{F}{5 - 4F} (C_{H_2} - 1) + \left[ \frac{F}{5 - 4F} \eta(H_2^+, H_2) + \frac{(1 - F)5}{5 - 4F} \eta(CO^+, H_2) \right]$$

the corresponding expression for CO desorption,  $\eta_M(CO)$ , being

$$\eta_M(CO) = \frac{5(1 - F)}{5 - 4F} (C_{CO} - 1) + \left[ \frac{F}{5 - 4F} \eta(H_2^+, CO) + \frac{(1 - F)5}{5 - 4F} \eta(CO^+, CO) \right]$$

Thus, the  $\eta$ 's measured in the ISR are dependent on the residual gas composition  $K^2$ ). Assuming  $C_{H_2} = C_{CO} \approx 0.1$  (see section 4.1) and using the relationships  $6.5\eta(H_2^+, H_2) = \eta(CO^+, H_2)$  and  $38\eta(H_2^+, CO) = \eta(CO^+, CO)$  the expressions for  $\eta_M(H_2)$  and  $\eta_M(CO)$  reduce to

$$\eta_M(H_2) = -\frac{0.9F}{5-4F} + \frac{F}{5-4F} \left[ \frac{5}{F} - 4.846 \right] \eta(CO^+, H_2)$$

and

$$\eta_M(CO) = -\frac{4.5(1-F)}{5-4F} + \frac{F}{5-4F} \left[ \frac{5}{F} - 4.974 \right] \eta(CO^+, CO)$$

In the laboratory (see section 3) what is measured is  $\eta(CO^+, H_2)$  and  $\eta(CO^+, CO)$  (more accurately  $\eta(^{15}N_2^+, H_2)$  and  $\eta(^{15}N_2^+, CO)$  but the difference is assumed to be small) both these quantities being  $\geq 0$ .

In figures 1 and 2 is shown the F dependence of  $\eta_M(H_2)$  and  $\eta_M(CO)$  for  $\eta_L(H_2)$  and  $\eta_L(CO)$  values of 1, 2 and 3 mol. ion<sup>-1</sup>. In the gas composition range applicable to the ISR, namely F between 0.9 and 0.95, it is seen that the measured ISR values  $\eta_M$  are quite different from those measured in the laboratory and strong functions of the gas composition.

When a surface has more than one adsorbed species, the measured desorption coefficient  $\eta_{\text{measured}}$  for a particular species is given by

$$\eta_{\text{measured}} = \eta(\theta = 1) \times \theta \quad (3)$$

where  $\theta(0 \leq \theta \leq 1)$  is the relative coverage of the species desorbed, thus a low  $\eta_{\text{measured}}$  implies either a low  $\theta$  or a low  $\eta(\theta = 1)$  or both.

### 3. EXPERIMENTAL

A schematic diagram of the apparatus is shown in figure 3.

The ion gun was of the electron impact type, and provided a current of  $4 \times 10^{-8}$  A between 0.5 and 3 keV at a pressure of  $2.0 \times 10^{-6}$  torr. Since CO( $m/e = 28$ ) is a normal residual gas component in UHV systems, nitrogen-15 was used in the ion source providing an ion beam  $^{15}\text{N}_2^+$  with a diameter  $\approx 40$  mm at the specimen.

Since ion induced changes in pressure  $\approx 10^{-10}$  torr are expected for an  $\eta_L = 1$ , a system of differential pumping was installed which reduced the pressure from  $2.0 \times 10^{-6}$  torr in the first stage to  $4 \times 10^{-9}$  torr in the measuring chamber.

The first two stages were pumped by a  $400 \text{ l s}^{-1}$  ion pump plus a liquid nitrogen cooled titanium sublimation pump, this combination giving a measured pumping speed of  $\approx 1800 \text{ l s}^{-1}$  for  $\text{H}_2$  and  $\approx 800 \text{ l s}^{-1}$  for  $\text{N}_2$ . Orifices of diameter  $\approx 2$  mm separated the first and second stages and the second stage and the measuring chamber.

Between the measuring chamber and a third identical ion pump - liquid nitrogen cooled titanium sublimation pump combination a tube of length 15.4 cm and diameter 3.9 cm provided a known conductance of  $132.3 \text{ l s}^{-1}$  for  $\text{H}_2$  and  $35, 36 \text{ l s}^{-1}$  for  $\text{N}_2$  and hence a known pumping speed in the measuring chamber.

Six samples ( $5 \times 5$  cm) at one time could be mounted on the rotatable sample holder and positioned in turn in front of the ion beam. This holder was held at + 30 V with respect to earth to suppress the effect of secondary electron emission on the measurement of the incident ion current.

Total pressure measurement was by Bayard-Alpert ionisation gauges, the gauge in the measuring chamber being calibrated against a standard available in the laboratory.

For partial pressure measurement a quadrupole mass spectrometer (Balzers model 111A) calibrated against the ionisation gauge was also mounted in the measuring chamber.

The complete system was bakeable to 300°C and after a 24 hour 300°C bakeout the base pressure in the measuring chamber was  $1 \times 10^{-10}$  torr.

The metals investigated were stainless steel (316 L + N), titanium alloy (73 Ti 13 V 11 Cr 3 Al) and pure aluminium. The stainless steel and the titanium samples were subjected to the complete cleaning procedure described in the Appendix whereas the pure aluminium samples passed through only the vapour degreasing bath.

For a measurement two samples of each metal were mounted in the system.

#### 4. RESULTS

##### 4.1 The re-emission probability C

Since  $N_2^{15}$  is not a normal surface contaminant of Al, Ti or stainless steel, the quantity C for  $N_2^{15}$  can be measured simply by tuning the quadrupole mass spectrometer to  $m/e = 30$  and measuring the desorption coefficient upon bombarding with  $^{15}N_2^+$  ions.

For all three materials C was found to be less than  $< 0.1$  for both baked and unbaked samples.

##### 4.2 Dependence of $\eta$ on bakeout time and temperature

The complete vacuum system containing the specimens was baked; thus, during bakeout the three materials were exposed to the same environment - namely the outgassing products of a stainless steel chamber and the usual components such as gauges and titanium sublimation pumps.

A set of six samples (two of each material) was cleaned and mounted in the vacuum system. After sufficient pumping time to reach a pressure  $\approx 1 \times 10^{-8}$  torr, usually three to four days, a measurement of  $\eta$  was made.

The system was then baked for, say, six hours at 300°C and  $\eta$  measured again.

To test the effect of a 12 hour 300°C bakeout completely new specimens were used, since it is not obvious that two 6 hour bakeouts give the same result as one 12 hour bakeout. Thus, for each bakeout, six completely new samples were used.

For all three materials investigated both before and after bakeout, bombardment by 2 keV  $^{15}\text{N}_2^+$  ions produced significant desorption of only four masses, 2 ( $\text{H}_2$ ), 16 ( $\text{CH}_4$ ), 28 (CO) and 44 ( $\text{CO}_2$ ).

Examination of the cracking patterns for our particular gas analyser revealed that mass 28 in our system was indeed CO and not  $^{14}\text{N}_2$ .

Figures 4, 5 and 6 show the partial  $\eta$ 's ( $=\eta_g$ ) for the four species desorbed from Ti, stainless steel and aluminium after 6, 12, 18 and 24 hour bakeouts at 300°C.

For all three materials the results are similar. There is a wide scatter in the measured  $\eta$ 's before bakeout, due, it is believed, to non reproducibility of the cleaning procedure. It must be remembered that the samples were not cleaned under controlled laboratory conditions but were treated as normal pieces of vacuum equipment and passed through the normal industrial cleaning baths and thus are hopefully representative of actual machine vacuum chambers.

Before bakeout,  $\eta_{\text{H}_2}$  and  $\eta_{\text{CO}}$  were the largest, followed by  $\eta_{\text{CO}_2}$  and  $\eta_{\text{CH}_4}$ .

Of the three materials, before bakeout, Al was marginally the dirtiest, a reflection of its only having been vapour degreased.

After 300°C bakeout, in general the longer the bakeout time, the lower the final  $\eta$  value, which, however, tended to an equilibrium value.

In the Ti even after 24 hours at 300°C,  $\eta_{\text{H}_2}$  was still about 3 mol. ion<sup>-1</sup> whereas for bakeout times from 12 hours to 24 hours,  $\eta_{\text{CO}_2}$  was always less than 0.1 mol. ion<sup>-1</sup> and  $\eta_{\text{CH}_4}$  was always below 0.2 mol. ion<sup>-1</sup>. In the case of  $\eta_{\text{CO}}$  it remained in the range of 1 to 2 mol. ion<sup>-1</sup>.

For bakeout times of 6 hours, higher  $\eta$  values were measured.

For stainless steel  $\eta_{H_2}$  and  $\eta_{CO}$  again tended to decrease with increasing bakeout times reaching values of between 0.6 and 1.7 mol. ion<sup>-1</sup> and 1.3 and 1.9 mol. ion<sup>-1</sup> respectively.

For bakeout times of 6, 12 and 18 hours  $\eta_{CO_2}$  and  $\eta_{CH_4}$  values between 0.2 and 0.3 mol. ion<sup>-1</sup> and 0.1 and 0.15 mol. ion<sup>-1</sup> respectively were obtained. After 24 hours at 300°C,  $\eta_{CO_2}$  reached 0.03 mol. ion<sup>-1</sup> whereas  $\eta_{CH_4}$  lay between 0.4 and 0.9 mol. ion<sup>-1</sup>.

Despite the fact that Al was dirtier than the Ti and stainless steel before bakeout, the 300°C bakeout tended to eliminate this difference. With increasing bakeout time  $\eta_{H_2}$  and  $\eta_{CO}$  decreased to values between 0.85 and 1.1 mol. ion<sup>-1</sup> and 0.9 and 1.15 mol. ion<sup>-1</sup> respectively.

Bakeout times of 18 hours and 24 hours gave  $\eta_{CO_2}$  values between 0.2 and 0.4 whereas 12 hour and 6 hour bakeouts gave rather higher values around 0.2 and 0.45 mol. ion<sup>-1</sup> respectively.

The  $\eta_{CH_4}$  values decreased from between 0.2 and 0.45 mol. ion<sup>-1</sup> for the 6 hour bakeout to between 0.04 and 0.05 mol. ion<sup>-1</sup> for the 24 hour bakeout.

It must be remembered that the total  $\eta$  is the sum of the four partial  $\eta$ 's. Not even after 24 hours at 300°C were any of the total  $\eta$ 's below 2 mol. ion<sup>-1</sup>.

The measurements were repeated for a bakeout temperature of 200°C and the results are shown in figures 7, 8 and 9 for Ti, aluminium and stainless steel respectively. Compared to a 300°C bakeout the 200°C bakeout is relatively inefficient in producing low  $\eta$  values. For all three metals increasing the time at 200°C from 6 hours to 24 hours did little, if anything, to reduce the  $\eta$  values. As, after the 300°C bakeout,  $\eta_{H_2}$  and  $\eta_{CO}$  were the largest, followed by  $\eta_{CO_2}$  and  $\eta_{CH_4}$ . In some samples of stainless steel and titanium  $\eta_{H_2}$  actually increased after bakeout!

The lowest  $\eta$  values obtained for Ti, Al and stainless steel respectively after 200°C bakeout - though not always after 24 hours were 2.3, 2.6 and 3.4 mol. ion<sup>-1</sup> for  $\eta_{H_2}$ , 0.15, 0.2 and 0.25 mol. ion<sup>-1</sup> for  $\eta_{CH_4}$ , 1.8, 2.75 and 2.95 mol. ion<sup>-1</sup> for  $\eta_{CO}$  and 0.4, 0.74 and 0.64 mol. ion<sup>-1</sup> for  $\eta_{CO_2}$ .

Total  $\eta$ 's of the order of 9 mol. ion<sup>-1</sup> can be expected after anything from 6 to 24 hours bakeout at 200°C.

#### 4.3 In situ pure argon discharge in unbaked system

Six samples were mounted in the measuring chamber and, after a suitable pumping time, the  $\eta$ 's were measured. The system was unbaked.

Pure argon was then introduced into the system to a pressure  $\approx 1 \times 10^{-2}$  torr and by applying - 400 V to the sample holder a gas discharge was initiated which caused the samples to be bombarded by argon ions of a few hundred eV energy. During the discharge the system was pumped by a turbomolecular pump and the argon flowed continuously.

Thermocouples attached to the specimens indicated that the Ti and Al samples reached  $\approx 220^\circ\text{C}$  while the stainless steel reached  $\approx 190^\circ\text{C}$ .

The ion dose received by the samples was calculated from the total current to the discharge. However, the actual area (samples + sample holder) bombarded by the discharge was difficult to estimate, thus the ion dose stated is only approximate.

Figures 10, 11 and 12 show the measured partial  $\eta$ 's for Ti, Al and stainless steel respectively, before and after in situ pure argon discharge. For clarity only, the results for one sample of each material have been shown.

For all three materials the results are similar. After normal cleaning and before discharge, the partial  $\eta$ 's have values similar to that quoted above.

After an argon ion dose of  $\approx 7.5 \times 10^{16}$  ions cm<sup>-2</sup> in all three materials,  $\eta_{H_2}$ ,  $\eta_{CO}$ ,  $\eta_{CH_4}$  and  $\eta_{CO_2}$  are at or below values normally obtained after 24 hours bakeout at 300°C.

However, argon has appeared in the desorption spectrum with  $\eta_A$  values of 0.26, 0.6 and 0.46 mol. ion<sup>-1</sup> for Ti, Al and stainless steel respectively.

Further argon discharge of the three materials with a total ion dose of  $\approx 8.3 \times 10^{17}$  ions cm<sup>-2</sup> results in samples with  $\eta_{H_2}$ ,  $\eta_{CH_4}$ ,  $\eta_{CO}$ , and  $\eta_{CO_2}$  below the limits of detection ( $< 0.01$  mol. ion<sup>-1</sup>). The sole species desorbed by the 2 keV  $^{15}N_2^+$  ions at this stage is argon with  $\eta_A$  values of 0.34 mol. ion<sup>-1</sup> for Ti, 0.18 mol. ion<sup>-1</sup> for Al and 0.29 mol. ion<sup>-1</sup> for stainless steel.

The base pressure  $\approx 1 \times 10^{-8}$  torr before and after discharge did not change appreciably, implying no change in pumping speed, and hence lower measured  $\eta$ 's, due to the possible pumping action of the clean sample surfaces. In addition, the measurements were not carried out until the following day; thus any pumping surface was well saturated by exposure to the  $1 \times 10^{-8}$  torr of unbaked system for  $\approx 24$  hours.

#### 4.4 In situ pure $^{14}N_2$ discharge in unbaked system

After in situ argon glow discharge there exists the risk that thermal degassing of argon gives a high argon partial pressure if the system is pumped only by titanium sublimation pumps and not by sputter ion pumps. To try to overcome this, it was decided to try an in situ glow discharge with pure  $^{14}N_2$  since any thermal outgassing of  $^{14}N_2$  after discharge is easily coped with by both titanium sublimation pumps and sputter ion pumps.

Again the results for all three materials are similar and for clarity only only the results from one sample of each material have been shown in Figures 13, 14 and 15 for Ti, Al and stainless steel respectively.

Compared to the in situ pure argon results,  $\eta_{CH_4}$  is reduced to  $< 0.01$  mol. ion<sup>-1</sup> after an ion dose of only  $\approx 7.5 \times 10^{16}$  ions cm<sup>-2</sup>. To reduce both  $\eta_{H_2}$  and  $\eta_{CO_2}$  to below this same level requires a dose  $\approx 1.6 \times 10^{18}$  ions cm<sup>-2</sup> and in the case of Al,  $\eta_{CO_2}$  was still measurable after this dose.

However, even after a dose of  $1.6 \times 10^{18}$  ions  $\text{cm}^{-2}$  mass 28 was still being desorbed from the surface in large quantities with  $\eta_{28}$  ranging from  $\approx 1.5$  mol. ion $^{-1}$  for stainless steel and Al to 2.4 mol. ion $^{-1}$  for Ti. The mass 28 was identified as  $^{14}\text{N}_2$  from its cracking pattern.

A subsequent pure argon discharge with a dose of  $\approx 7.5 \times 10^{17}$  ions  $\text{cm}^{-2}$  was sufficient to reduce  $\eta_{28}$  ( $= \eta_{\text{N}_2}$ ) to 0.18 mol. ion $^{-1}$  in Ti, 0.15 mol. ion $^{-1}$  in stainless steel and to below 0.01 mol. ion $^{-1}$  in Al. In addition,  $\eta_A$  became apparent being 0.11,  $< 0.01$  and 0.22 mol. ion $^{-1}$  in Ti, Al and stainless steel respectively.

It is interesting to note that after the pure  $^{14}\text{N}_2$  discharge, the residual gas composition had changed from that of a normal unbaked stainless steel system, i.e. mass 18 ( $\text{H}_2\text{O}$ ) predominating, to a spectrum whose two largest peaks occurred at 16 ( $\text{NH}_2$ ) and 17 ( $\text{NH}_3$ ). An additional small peak appeared at mass 27 ( $\text{C}_2\text{H}_3$  or  $\text{CNH}$ ). However, after some hours pumping the spectrum returned to normal.

Using the equipment described in reference 4, the surface of a sample of stainless steel was analysed via Auger electron spectroscopy before and after  $\text{N}_2$  discharge in an unbaked system without exposing the sample to air. The results are shown in Figure 16 where the top Auger spectrum before  $\text{N}_2$  discharge reveals a stainless steel surface with a relatively large C surface contamination. After a nitrogen ion dose  $\approx 1.6 \times 10^{18}$  ions  $\text{cm}^{-2}$ , the bottom Auger spectrum was recorded. The  $\text{N}_2$  discharge has practically removed the C contamination and also the oxide passivation layer as seen by the diminution of the oxygen peak, but a large nitrogen peak is now evident corresponding to an  $\text{N}_2$  surface concentration of  $\approx 45$  at. %. It was not possible to say whether the nitrogen was in the form of nitride or simply implanted gas, but whatever its chemical state, it is certainly this nitrogen which was responsible for the continued high desorption of mass 28 from a similarly treated surface.

Only stainless steel was studied but it is expected that Al and Ti would show similar results.

#### 4.5 In situ pure argon discharge in baked system

Six samples were placed in the  $\eta$  measuring apparatus and the  $\eta$ 's measured before and after a 24 hour 300°C bakeout.

To check the effect of an air leak on  $\eta$  after bakeout, air was admitted to the system via a leak valve, to a pressure of  $2 \times 10^{-8}$  torr for 12 hours; then the system was repumped but not baked.

The results are shown in figures 17, 18 and 19 where for clarity only the results from one sample of each material are shown. For all three materials (6 samples) after the 12 hour  $5 \times 10^{-8}$  torr air leak,  $\eta_{H_2}$  and  $\eta_{CH_4}$  have all increased by as much as 50% in some samples but nevertheless the values are still below that of the completely unbaked state.

In four of the six samples (2 Ti, 1 Al and 1 stainless steel)  $\eta_{CO_2}$  decreased while in the remaining two (Al and stainless steel) it increased. In all six samples  $\eta_{CO}$  decreased.

A subsequent in situ pure argon discharge of  $8.5 \times 10^{17}$  ions  $cm^{-2}$  resulted in clean samples with only mass 40 (argon) being desorbed. For Ti, Al and stainless steel respectively, the  $\eta_A$  values were 0.12 and 0.12, 0.077 and 0.067 and 0.09 and 0.067 mol. ion<sup>-1</sup>.

A subsequent 300°C 24 hour bakeout without going up to air resulted in a decrease in  $\eta_A$  for all three materials. In the case of stainless steel,  $\eta_A$  became  $< 0.01$  mol. ion<sup>-1</sup>.

A recontamination of CO occurred in all three materials and in addition H<sub>2</sub> reappeared on both Al samples. However, the total  $\eta$  was still well below 1 mol. ion<sup>-1</sup> being 0.16 and 0.17 mol. ion<sup>-1</sup> for Ti, 0.21 and 0.62 mol. ion<sup>-1</sup> for Al and 0.16 and 0.17 mol. ion<sup>-1</sup> for stainless steel.

An exposure to air of 12 hours resulted in a recontamination of all three metals; however, in Ti and Al the CO<sub>2</sub> was absent ( $\eta_{CO_2} < 0.01$  mol. ion<sup>-1</sup>). The total recontamination was always less than the unbaked state (after cleaning) but more than the 24 hour 300°C bakeout state. In all three materials  $\eta_{CO}$  predominated, followed by  $\eta_{H_2}$  and  $\eta_{CH_4}$ . Only in the stainless steel sample was  $\eta_{CO_2}$  detectable.

A subsequent 24 hour 300°C bakeout reduced  $\eta_{H_2}$ ,  $\eta_{CO}$  and  $\eta_{CH_4}$  in all three metals but  $\eta_{CO_2}$  reappeared in the Ti and the pure Al while becoming  $< 0.01 \text{ mol. ion}^{-1}$  in the stainless steel. In all three metals both  $\eta_{H_2}$  and  $\eta_{CO}$  were reduced to less than  $1 \text{ mol. ion}^{-1}$ ,  $\eta_A$ ,  $\eta_{CH_4}$  and  $\eta_{CO_2}$  being at least a factor of ten lower. For the Ti, the Al and the stainless steel, the total  $\eta$ 's were 1.39, 0.88 and  $1.31 \text{ mol. ion}^{-1}$  respectively, values much better than could ever be achieved by a normal 24 hour 300°C bakeout.

#### 4.6 External argon/10% oxygen discharge

It has been shown<sup>4)</sup> that addition of 10% oxygen to the argon gas results in more efficient removal of C from the surface of stainless steel as judged by Auger electron spectroscopy.

Four samples of stainless steel were cleaned and two identical ISR vacuum chambers were set up for discharge cleaning in parallel as described in reference 4. Two samples of stainless steel were placed in each vacuum chamber. Both chambers were heated to 300°C and both were filled to  $\approx 10^{-2}$  torr of argon/10% oxygen, but only one chamber was discharged, the other acting as a control. After a dose of  $\approx 1 \times 10^{18} \text{ ions cm}^{-2}$  the discharge was stopped and the temperature of both chambers raised to 350°C for 10 hours to deplete the argon implanted in the surface layers by the discharge<sup>7)</sup>. The samples were removed from the vacuum chambers and mounted in the  $\eta$  measuring equipment.

The results are shown in figure 20 where, for clarity, only the results from one control sample and one discharged sample are displayed. It is seen that after discharge  $\eta_{H_2}$ ,  $\eta_{CO}$ ,  $\eta_{CO_2}$ , and  $\eta_{CH_4}$  are all lower than in the control sample; in addition, argon is being desorbed with  $\eta_A \approx 0.09 \text{ mol. ion}^{-1}$ .

After a 24 hour 300°C bake in the  $\eta$  machine on the discharged sample,  $\eta_{CO}$  is  $0.49 \text{ mol. ion}^{-1}$ ,  $\eta_{H_2}$  is  $0.2 \text{ mol. ion}$  and  $\eta_{CO_2}$ ,  $\eta_{CH_4}$ , and  $\eta_A$  are all  $< 0.04 \text{ mol. ion}^{-1}$ , whereas  $\eta_{CO}$  remains  $\approx 1 \text{ mol. ion}^{-1}$  and

$\eta_{H_2} \approx 0.75 \text{ mol. ion}^{-1}$  with  $\eta_{CO_2}$  and  $\eta_{CH_4} \approx 0.04 \text{ mol. ion}^{-1}$  in the control sample.

On the control sample there was no trace of argon.

#### 4.7 The energy dependence of $\eta$

Figure 21 shows the energy dependence of the four partial  $\eta$ 's for energies between 0.5 and 3 keV. These results are for an unbaked sample and are similar for all three materials. After bakeout the same form of the curve is observed but, of course, with correspondingly lower  $\eta$  values.

The desorption coefficient increases smoothly within the energy range 0.5 to 3 keV but the curve tends to be flattening out beyond 3 keV, the overall shape being in agreement with the energy dependence of sputtering yields of bulk materials<sup>5)</sup>. The curves do not pass identically through zero since there is a threshold energy for desorption of the order of a few eV<sup>6)</sup>.

### 5. CONCLUSIONS

For 2 keV  $^{15}N_2^+$  ions the re-emission probability  $C$  is found to be  $< 0.1$  for both baked and unbaked samples of Ti, Al and stainless steel.

A 300°C, 24 hour bakeout of these three materials is sufficient to reduce both  $\eta_{CO_2}$  and  $\eta_{CH_4}$  to less than 0.1 mol. ion<sup>-1</sup> but both  $\eta_{H_2}$  and  $\eta_{CO}$  remain high  $\approx 1 \text{ mol. ion}^{-1}$ . Bakeouts of shorter times give correspondingly higher values. Total  $\eta$ 's of the order of 5 mol. ion<sup>-1</sup> were measured.

A 200°C bakeout is less efficient with all  $\eta$ 's correspondingly higher. Both  $\eta_{H_2}$  and  $\eta_{CO}$  were  $\approx 3$  to 4 mol. ion<sup>-1</sup> after 24 hours at 200°C with  $\eta_{CO_2} \approx 0.8 \text{ mol. ion}^{-1}$  and  $\eta_{CH_4} \approx 0.2 \text{ mol. ion}^{-1}$ . Total  $\eta$ 's  $\approx 9 \text{ mol. ion}^{-1}$  were measured.

On unbaked samples total  $\eta$ 's  $\approx 20 \text{ mol. ion}^{-1}$  were measured. In general  $\eta_{H_2}$  and  $\eta_{CO}$  are  $\approx 10$  times  $\eta_{CO_2}$  and  $\eta_{CH_4}$  irrespective of bakeout temperature or time and are thus the major contributors to pressure instabilities in systems subjected to ion bombardment.

It is tempting to interpret the relatively low  $\eta_{\text{CO}_2}$  and  $\eta_{\text{CH}_4}$  values as being due to a low surface coverage of these species but this is not necessarily the case since the measured  $\eta$  is the product of the surface concentration of the species in question and the desorption efficiency for complete coverage (equation 3).

Since  $\eta(28^+,2) \approx 6.5\eta(2^+,2)$ ,  $\eta(28^+,16) = 4\eta(2^+,16)$ ,  $\eta(28^+,28) = 38\eta(2^+,28)$  and  $\eta(28^+,44) = 30\eta(2^+,44)$  at 5 keV after a 24 h, 300°C bake<sup>3)</sup>, where  $\eta(a^+,b)$  is the  $\eta$  for ion  $a^+$  desorbing molecule  $b$ , (in this notation the  $\eta$ 's quoted in this report are for  $a^+ = 30^+$ ) it is important to keep the mass of the bombarding ion low which implies a residual vacuum containing as high a percentage of  $\text{H}_2$  as possible. In addition, a low surface coverage of high mass molecules is preferred, especially CO since more CO than  $\text{CH}_4$  or  $\text{CO}_2$  is desorbed, to reduce their desorption, subsequent ionisation and hence more efficient desorption.

Before bakeout, the Al was marginally dirtier than the Ti and stainless steel since it was only vapour degreased. After bakeout all three materials showed similar  $\eta$ 's probably due to an equilibrium being reached between the residual gas and all the sample surfaces.

In situ pure argon discharge in an unbaked system reduces  $\eta_{\text{H}_2}$ ,  $\eta_{\text{CH}_4}$ ,  $\eta_{\text{CO}}$  and  $\eta_{\text{CO}_2}$  to less than 0.01 mol. ion<sup>-1</sup> but leaves an  $\eta_{\text{A}} \approx 0.3$  mol. ion<sup>-1</sup> which is a total  $\eta$  more than an order of magnitude lower than can be achieved with a 24 hour, 300°C bakeout. An ion dose  $\approx 8.3 \times 10^{17}$  ions cm<sup>-2</sup> was required.

An in situ pure  $\text{N}_2$  discharge in an unbaked system proved unsuccessful with  $\eta_{28}$ 's of the order of 2 to 3 mol. ion<sup>-1</sup> even after an ion dose of  $\approx 1.6 \times 10^{18}$  ions cm<sup>-2</sup> but, nevertheless reduced  $\eta_{\text{H}_2}$ ,  $\eta_{\text{CH}_4}$  and  $\eta_{\text{CO}_2}$  to below 0.01 mol. ion<sup>-1</sup>. A subsequent pure argon discharge reduced the  $\eta_{28}$  to less than 0.01 mol. ion<sup>-1</sup> in Al and to about 0.2 mol. ion<sup>-1</sup> in the Ti and stainless steel but as before, left each sample with an  $\eta_{\text{A}}$  between 0.15 and 0.4 mol. ion<sup>-1</sup>.

Analysis of a nitrogen discharged stainless steel specimen via Auger electron spectroscopy revealed a large surface concentration of nitrogen  $\approx 45$  at. % which was certainly the source of the mass 28 desorbed. The chemical state of the nitrogen was unknown.

An in situ pure argon discharge after a 24 hour, 300°C bakeout is also very effective in reducing  $\eta_{H_2}$ ,  $\eta_{CH_4}$ ,  $\eta_{CO}$  and  $\eta_{CO_2}$  to less than 0.01 mol. ion<sup>-1</sup> with once more the appearance of an  $\eta_A$  between 0.1 and 0.07 mol. ion<sup>-1</sup>.

A subsequent 24 hour, 300°C bakeout does not recontaminate the surfaces to a very great extent. In the Ti and stainless steel samples, only  $\eta_{CO}$  reappears to about 0.15 mol. ion<sup>-1</sup> but in Al  $\eta_{H_2}$  appears at 0.15 mol. ion<sup>-1</sup> and  $\eta_{CO}$  to about 0.06 mol. ion<sup>-1</sup> - surfaces which are still, however, about an order of magnitude cleaner than after 24 hours at 300°C.

Stainless steel samples, glow discharge cleaned with argon/10% oxygen as part of the standard cleaning procedure of the ISR vacuum chambers, showed a total  $\eta$  of 2.46 mol. ion<sup>-1</sup> after this treatment whereas a non-discharged control sample had a total  $\eta$  of 6.06 mol. ion<sup>-1</sup>. After baking at 300°C for 24 hours the discharged sample had a total  $\eta$  of 0.76 mol. ion<sup>-1</sup>,  $\eta_{CO}$  being the largest at 0.49 mol. ion<sup>-1</sup> compared to a total  $\eta$  of 1.86 mol. ion<sup>-1</sup> with  $\eta_{CO} = 1.04$  mol. ion<sup>-1</sup> for the undischarged control sample.

#### ACKNOWLEDGEMENTS

The author is indebted to Drs. Blechschmidt, Calder, Fischer, Gröbner and Hilleret for useful discussion and to Mr. A. Grillot for valuable technical assistance.

#### APPENDIX

The chemical cleaning procedure consisted of the following steps :

1. Perchloroethylene vapour degreasing at 121°C
2. Ultrasonic cleaning in alkaline detergent solution at 65°C
3. Rinsing in cold demineralised water
4. Drying in a hot air oven at 150°C.

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FIGURE CAPTIONS

1. The measured  $\eta$  in the ISR for desorption of  $H_2$ ,  $\eta_M$ , as a function of residual gas composition F for  $\eta_L$  values of 1, 2 and 3 mol. ion<sup>-1</sup>.
2. The measured  $\eta$  in the ISR for desorption of CO,  $\eta_M$ , as a function of residual gas composition F for  $\eta_L$  values of 1, 2 and 3 mol. ion<sup>-1</sup>.
3. Schematic diagram of the apparatus.
4. The desorption coefficient  $\eta$  for Ti alloy as a function of bakeout time at 300°C.
5. The desorption coefficient  $\eta$  for pure Al as a function of bakeout time at 300°C.
6. The desorption coefficient  $\eta$  for stainless steel as a function of bakeout time at 300°C.
7. The desorption coefficient  $\eta$  for Ti alloy as a function of bakeout time at 200°C.
8. The desorption coefficient  $\eta$  for pure Al as a function of bakeout time at 200°C.
9. The desorption coefficient  $\eta$  for stainless steel as a function of bakeout time at 200°C.
10. The effect on  $\eta$  for Ti alloy of an in situ pure A glow discharge in an unbaked system.
11. The effect on  $\eta$  for pure Al of an in situ pure A glow discharge in an unbaked system.
12. The effect on  $\eta$  for stainless steel of an in situ pure A glow discharge in an unbaked system.
13. The effect on  $\eta$  for Ti alloy of an in situ pure  $N_2$  glow discharge in an unbaked system.
14. The effect on  $\eta$  for pure Al of an in situ pure  $N_2$  glow discharge in an unbaked system.
15. The effect on  $\eta$  for stainless steel of an in situ pure  $N_2$  glow discharge in an unbaked system.
16. Auger spectra of stainless steel before (top) and after (bottom) pure  $N_2$  discharge.
17. The effect on  $\eta$  for Ti alloy of an air leak after 24 hours at 300°C followed by an in situ pure A glow discharge, then another 24 hour 300°C bakeout, an exposure to air, and a third 24 hour 300°C bakeout.

18. The effect on  $\eta$  for pure Al of an air leak after 24 hours at 300°C followed by an in situ pure A glow discharge, then another 24 hour 300°C bakeout, an exposure to air and a third 24 hour 300°C bakeout.
19. The effect on  $\eta$  for stainless steel of an air leak after 24 hours at 300°C followed by an in situ pure A glow discharge, then another 24 hour 300°C bakeout, an exposure to air and a third 24 hour 300°C bakeout.
20. The effect of an external argon/10% oxygen discharge on stainless steel.
21. The energy dependence of  $\eta$ .



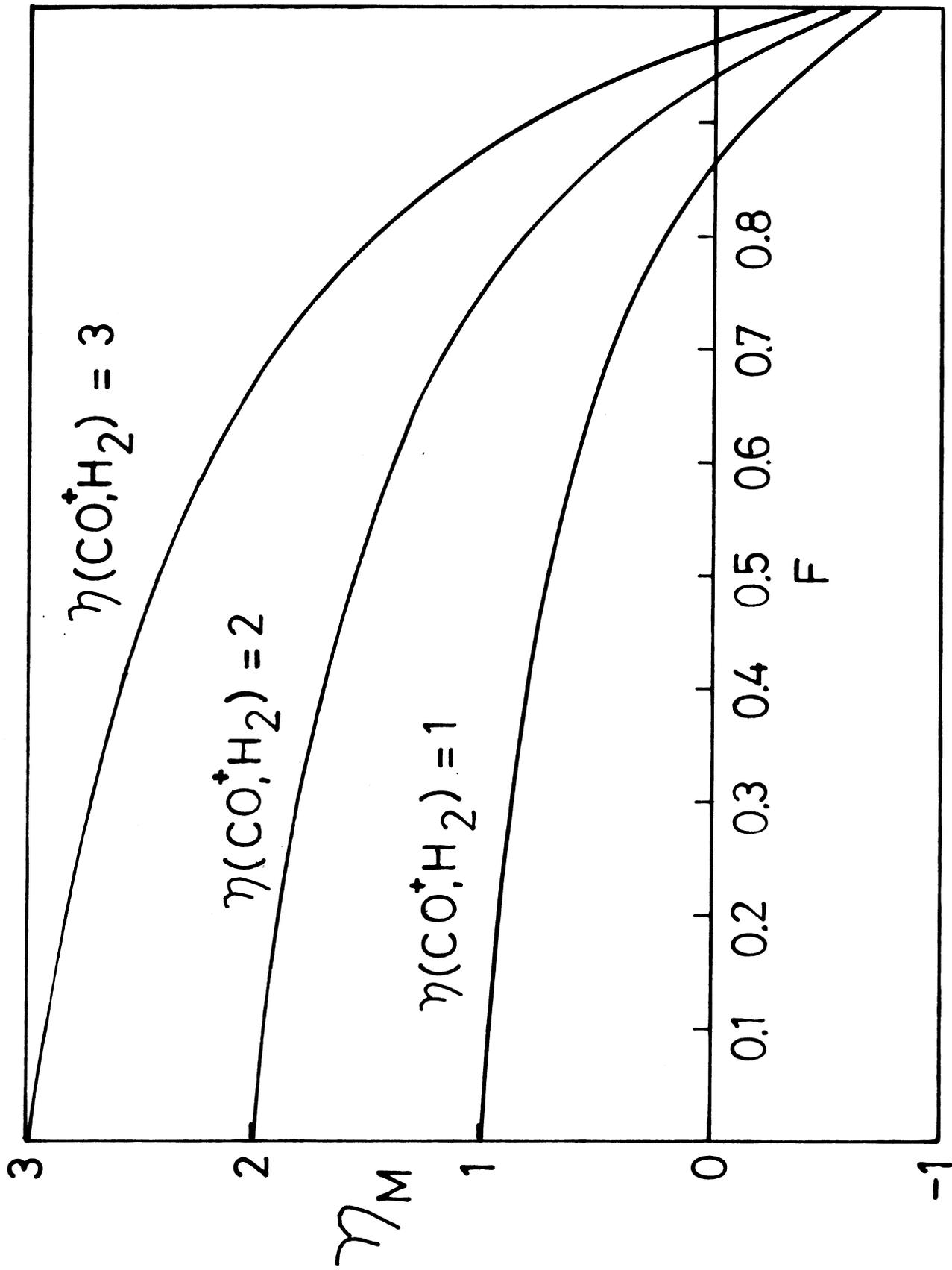


Figure 1

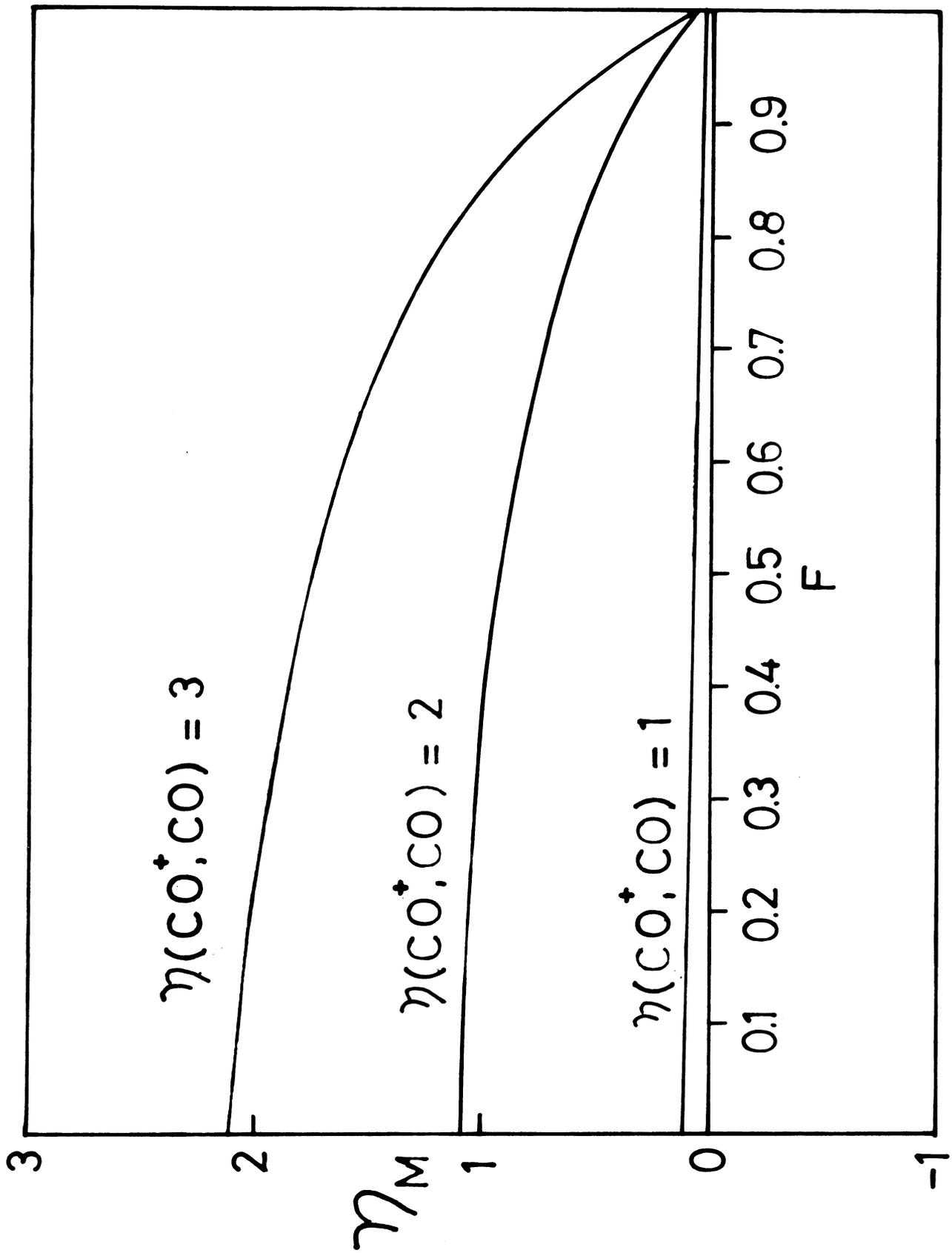


Figure 2

# QUADRUPOLE

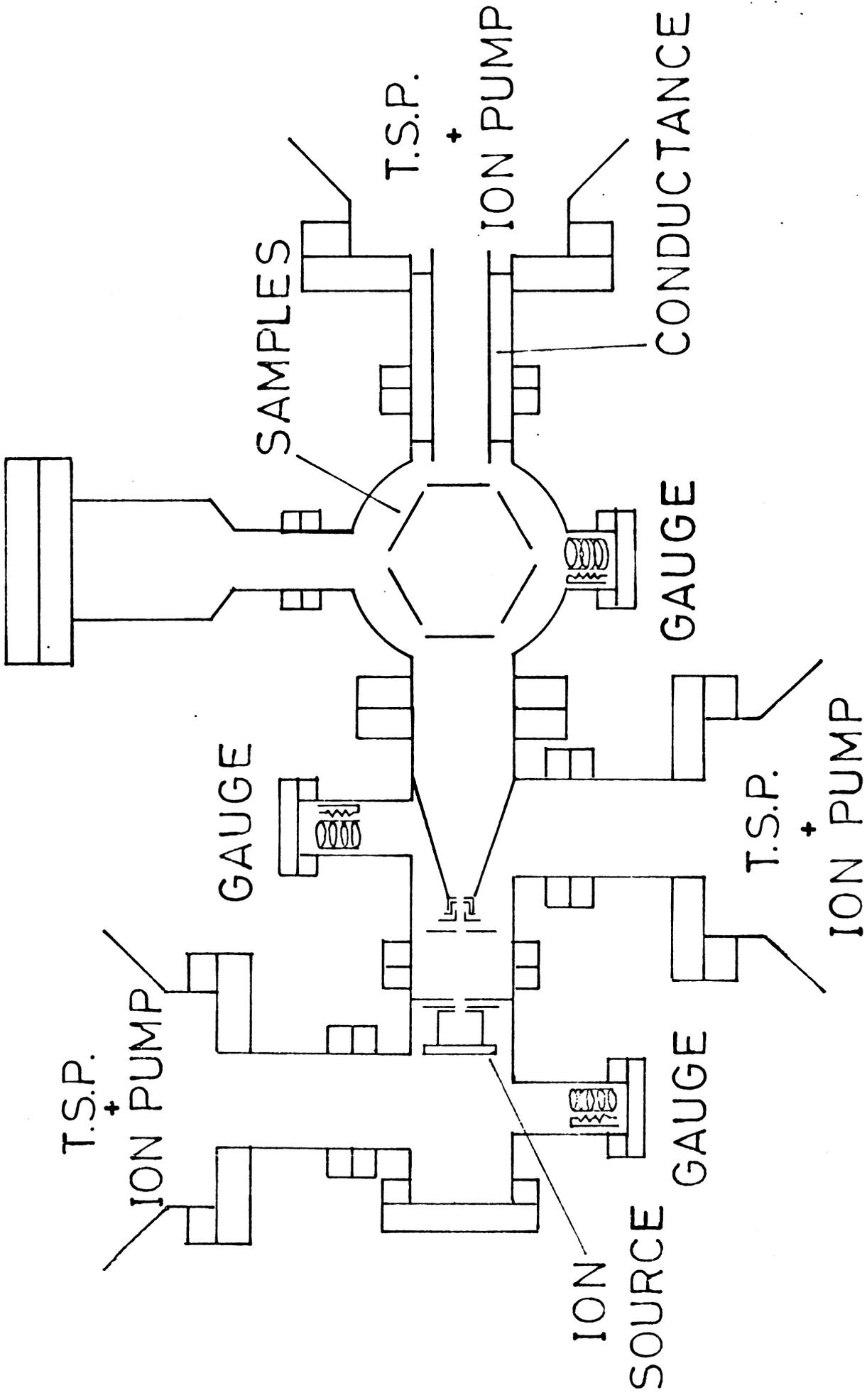


Figure 3

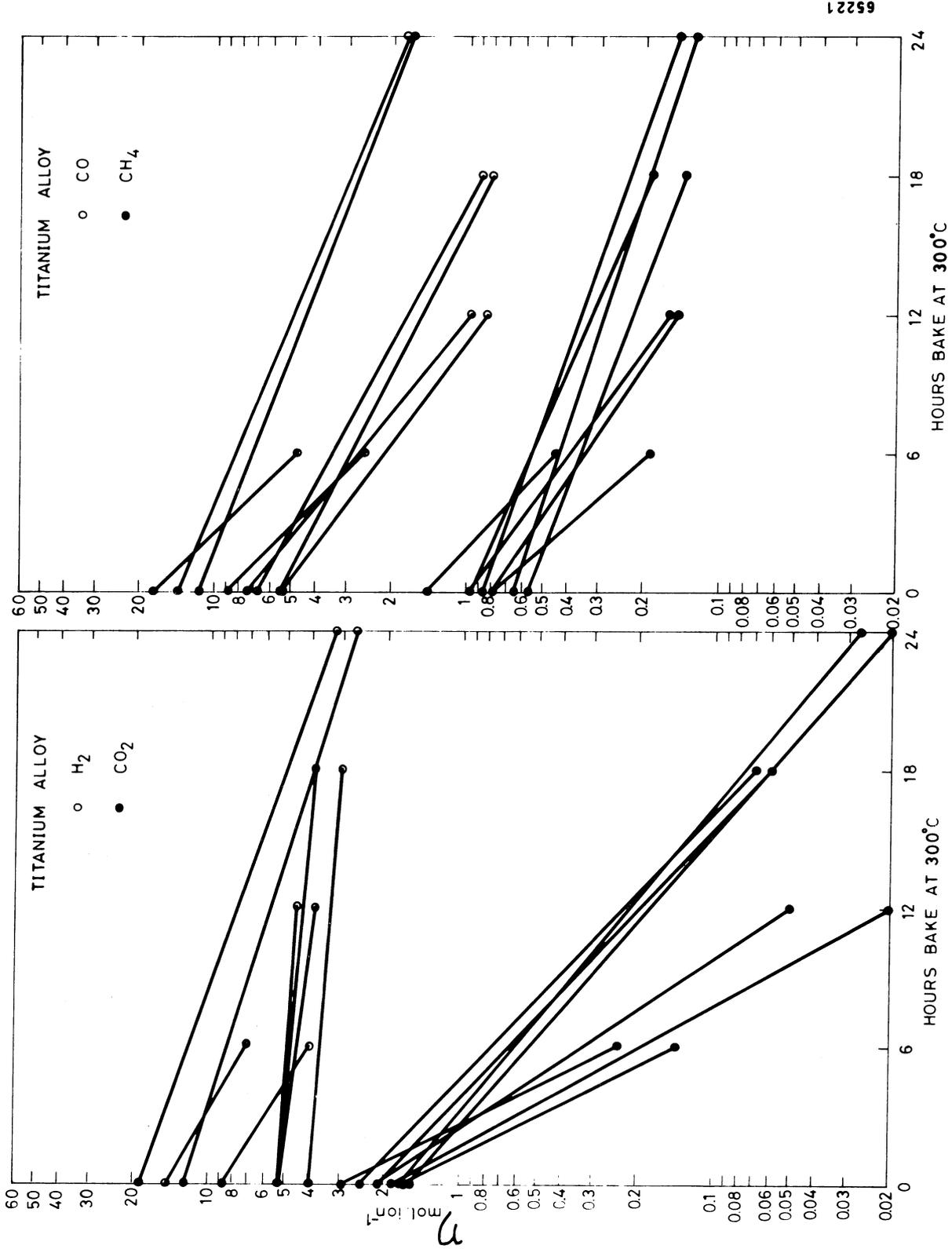


Figure 4

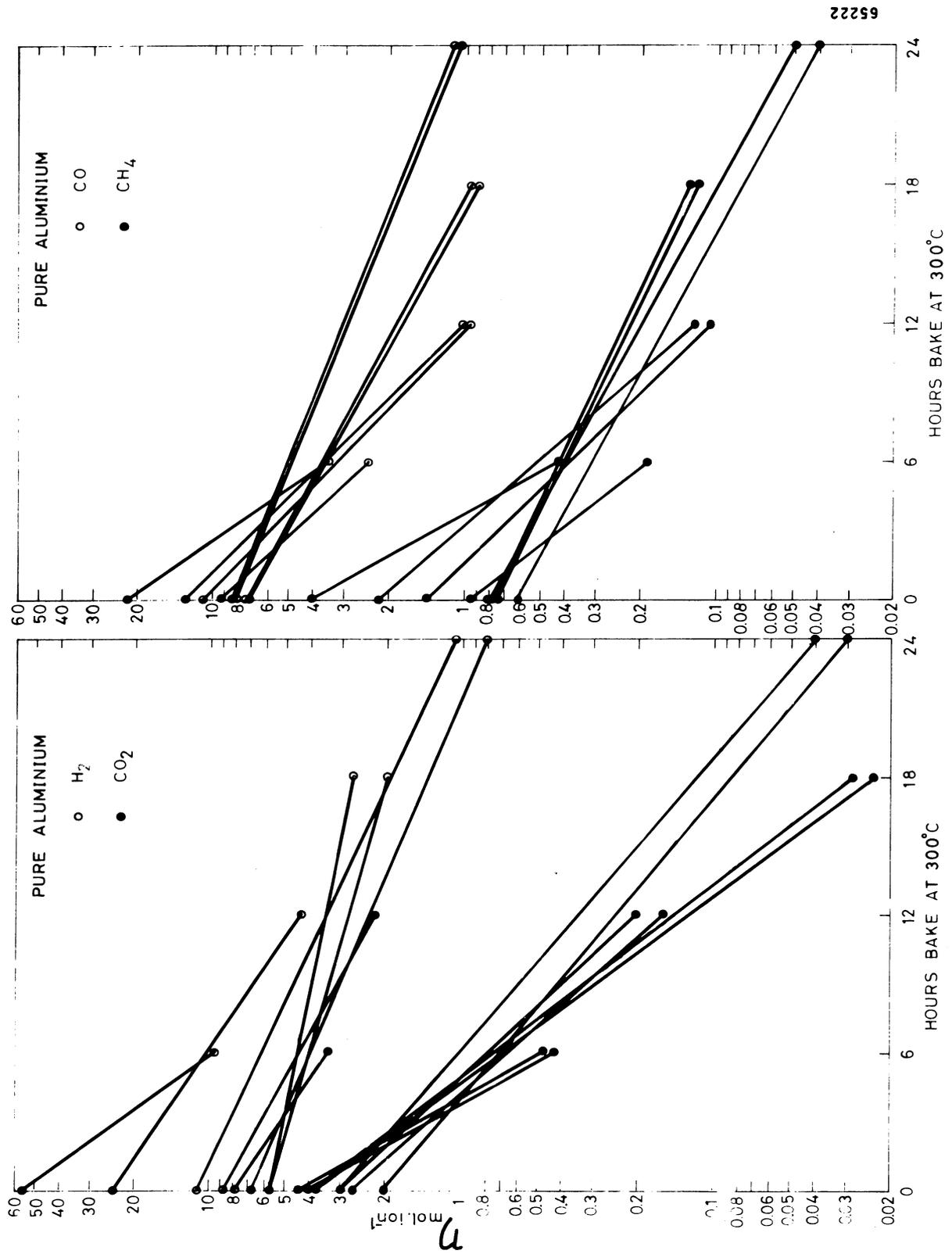


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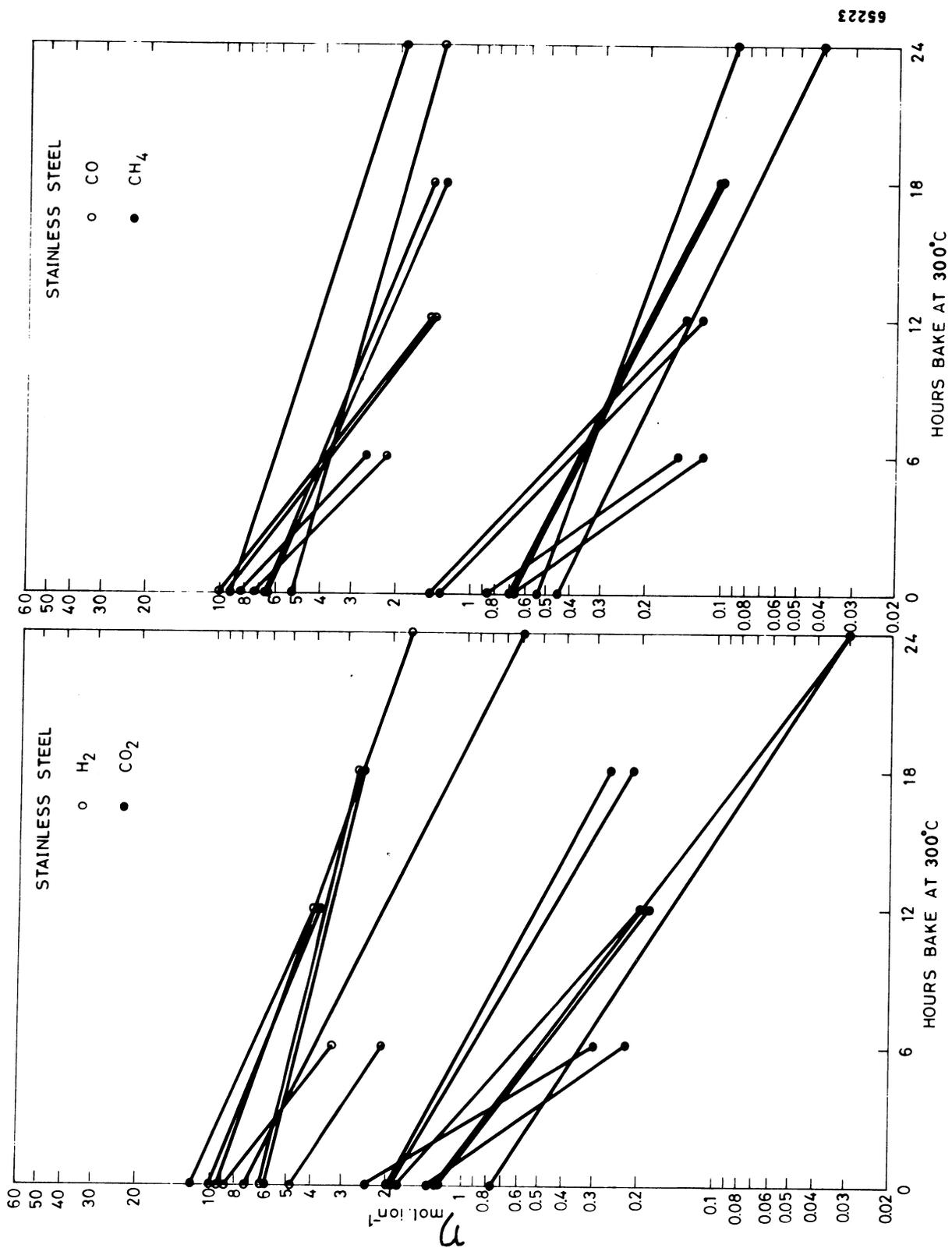


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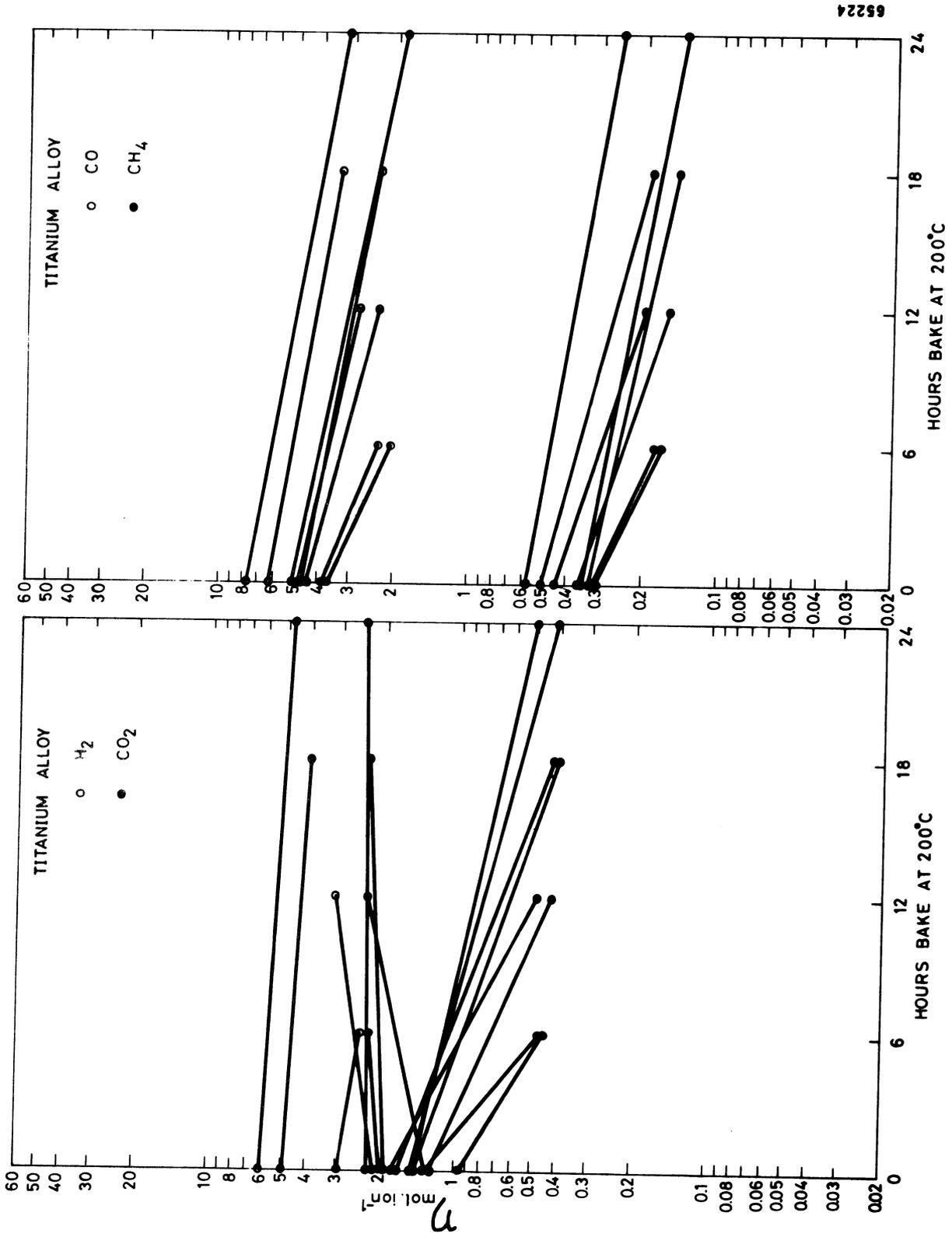
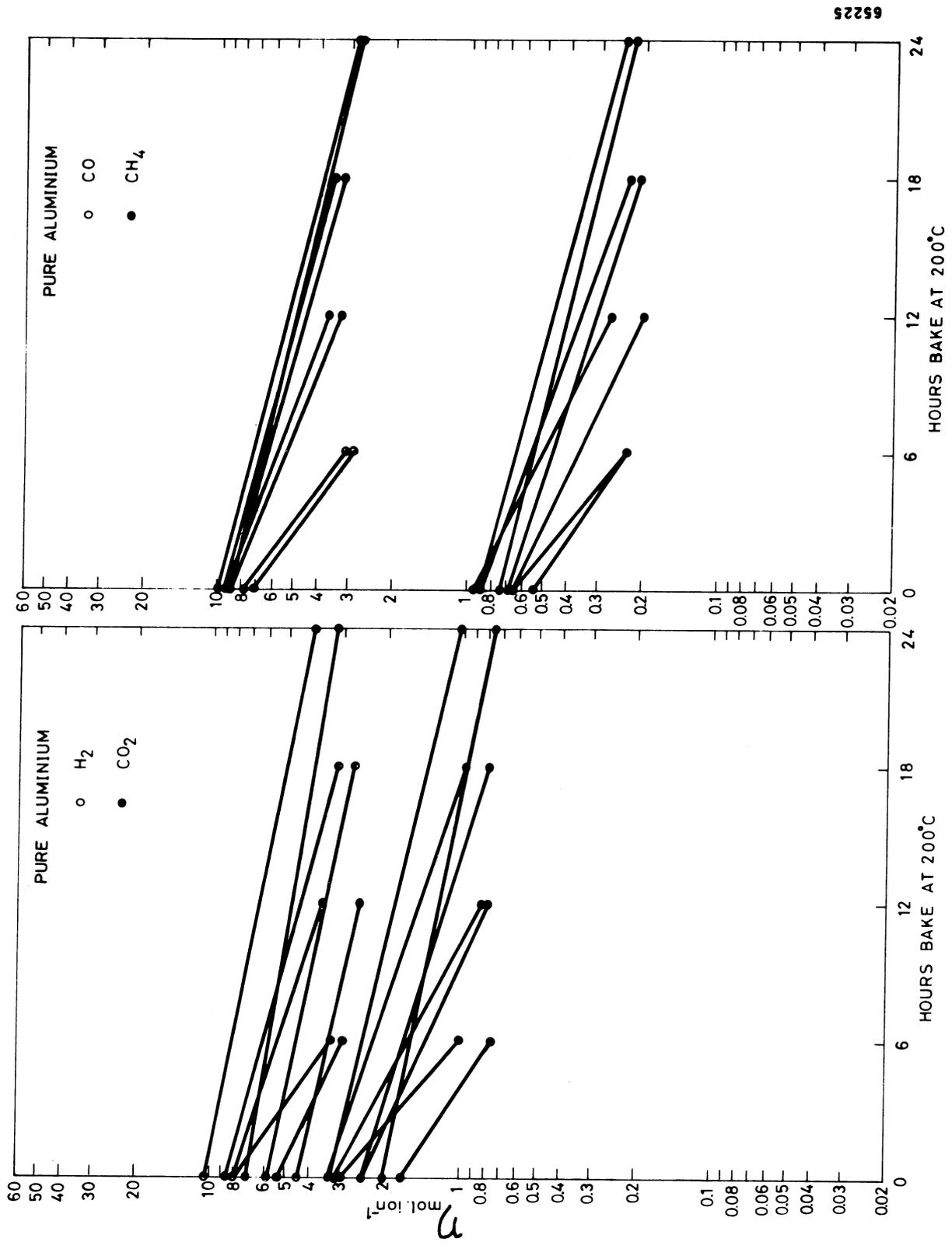


Figure 7



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Figure 8

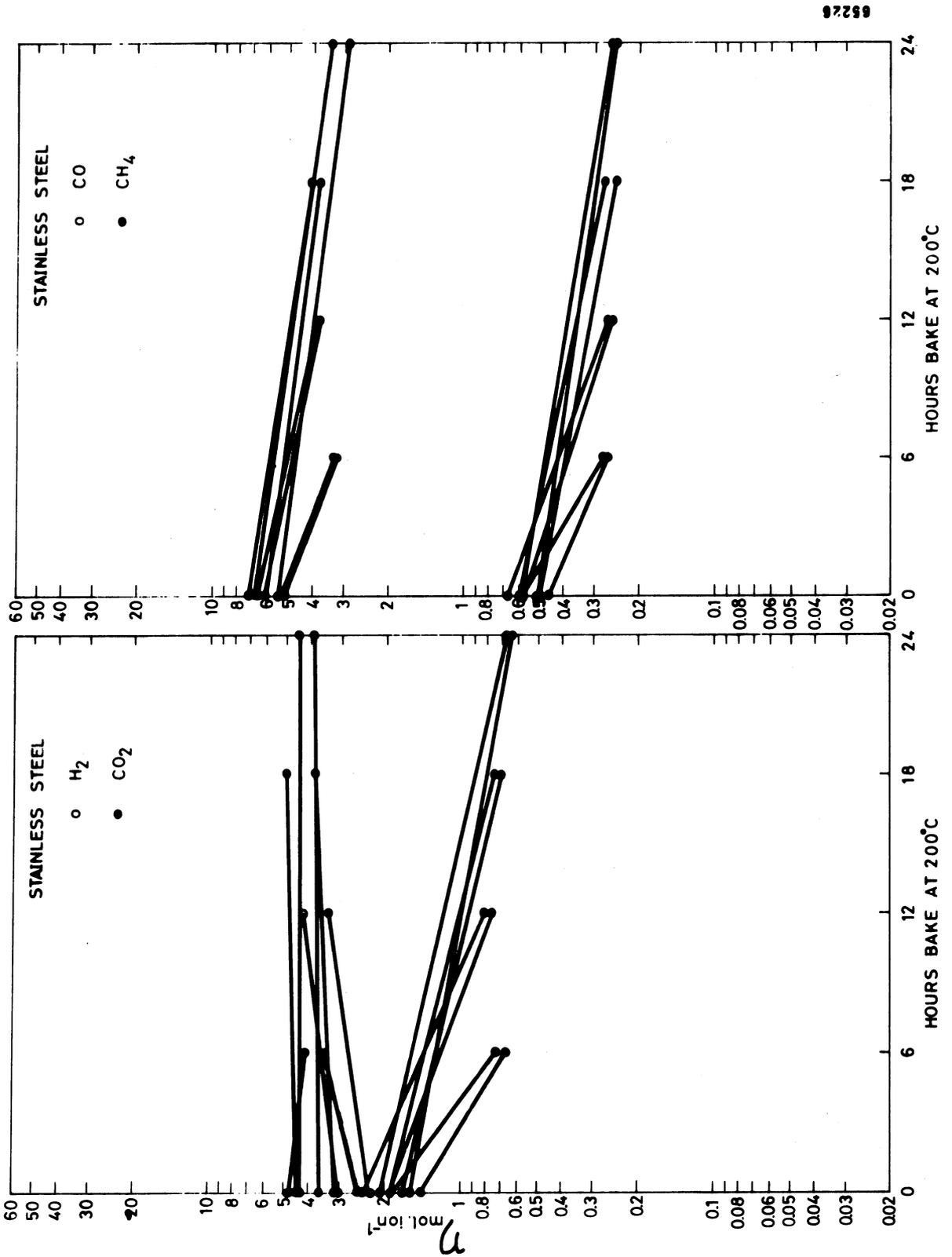


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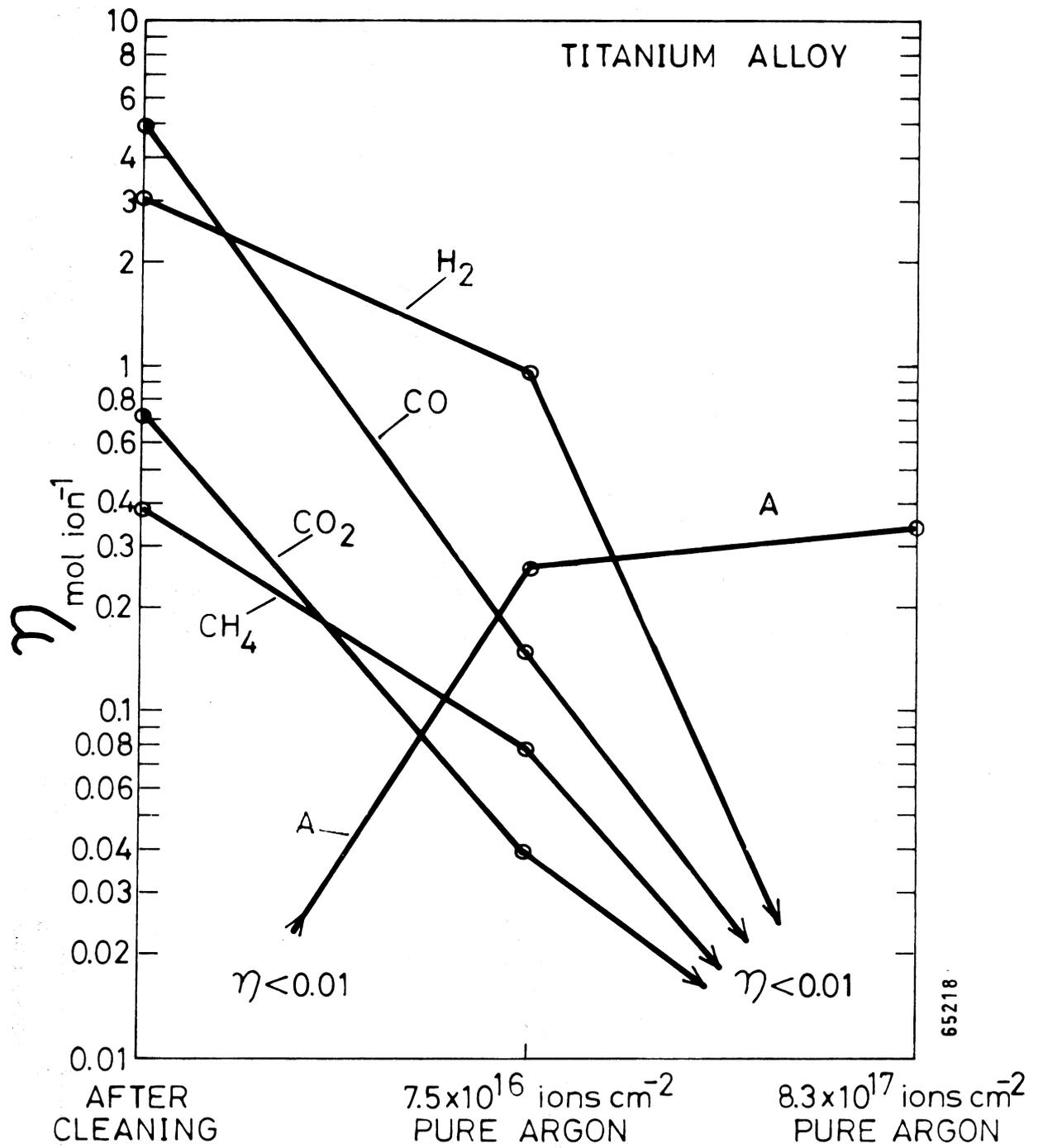


Figure 10

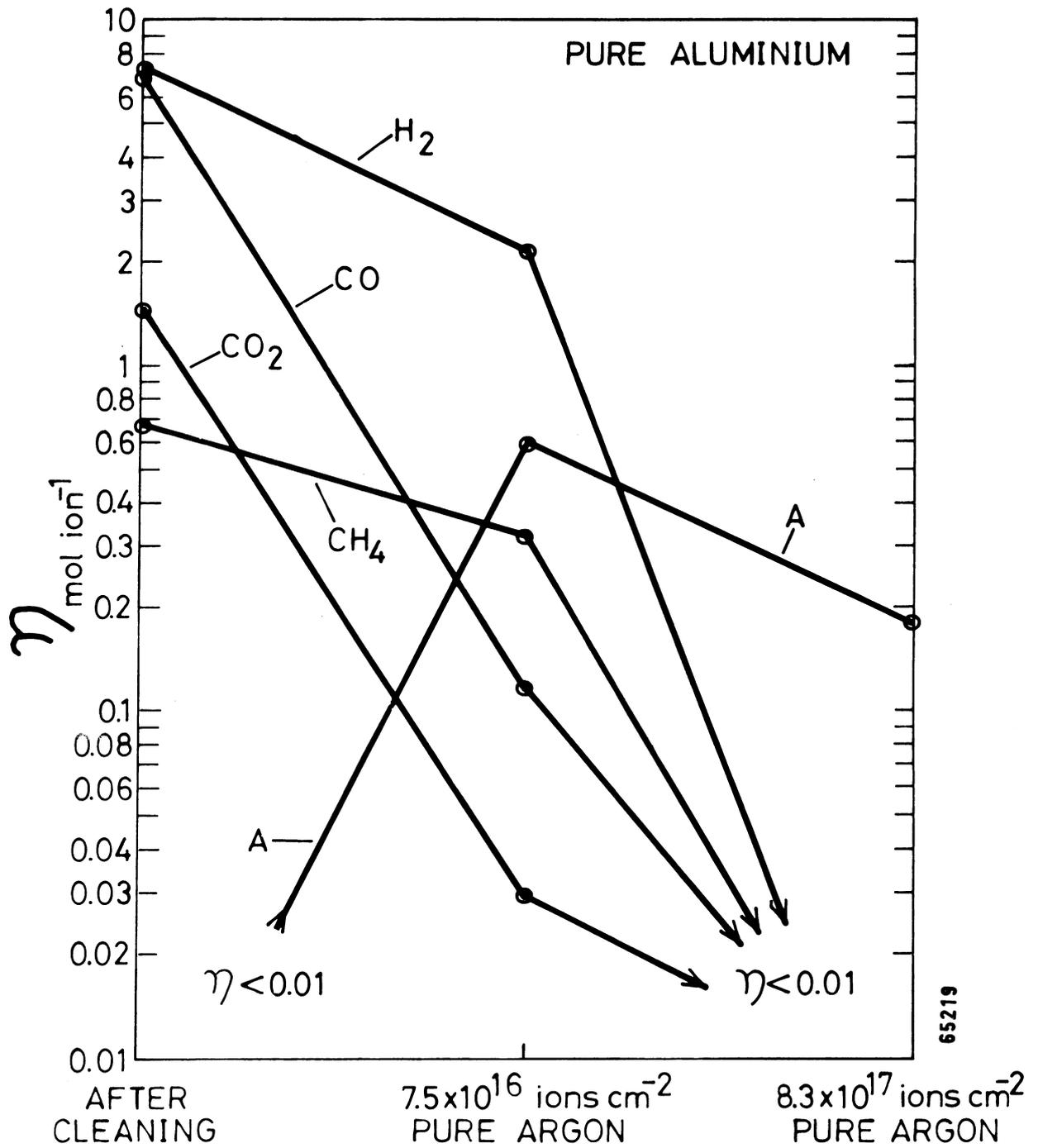


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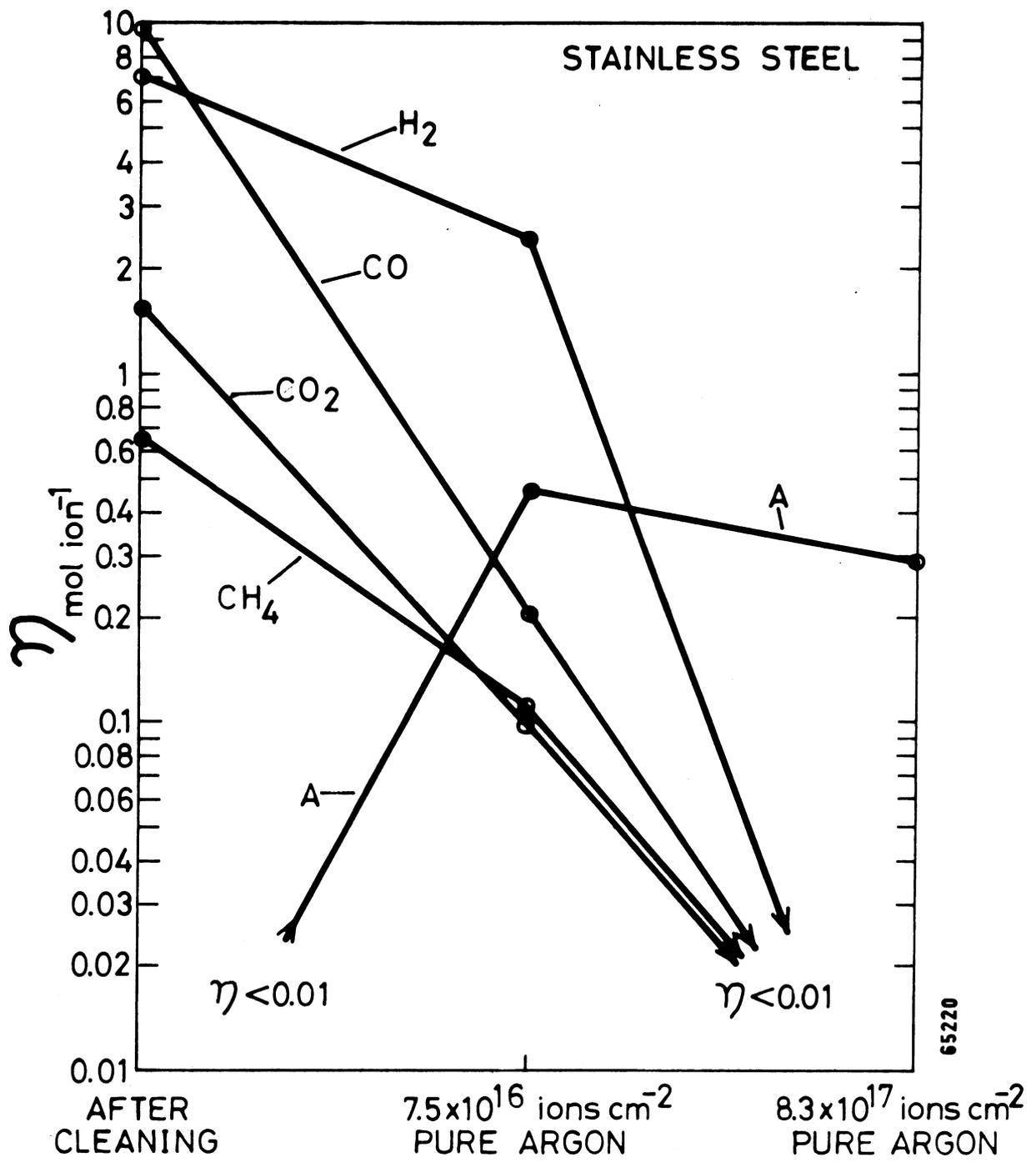


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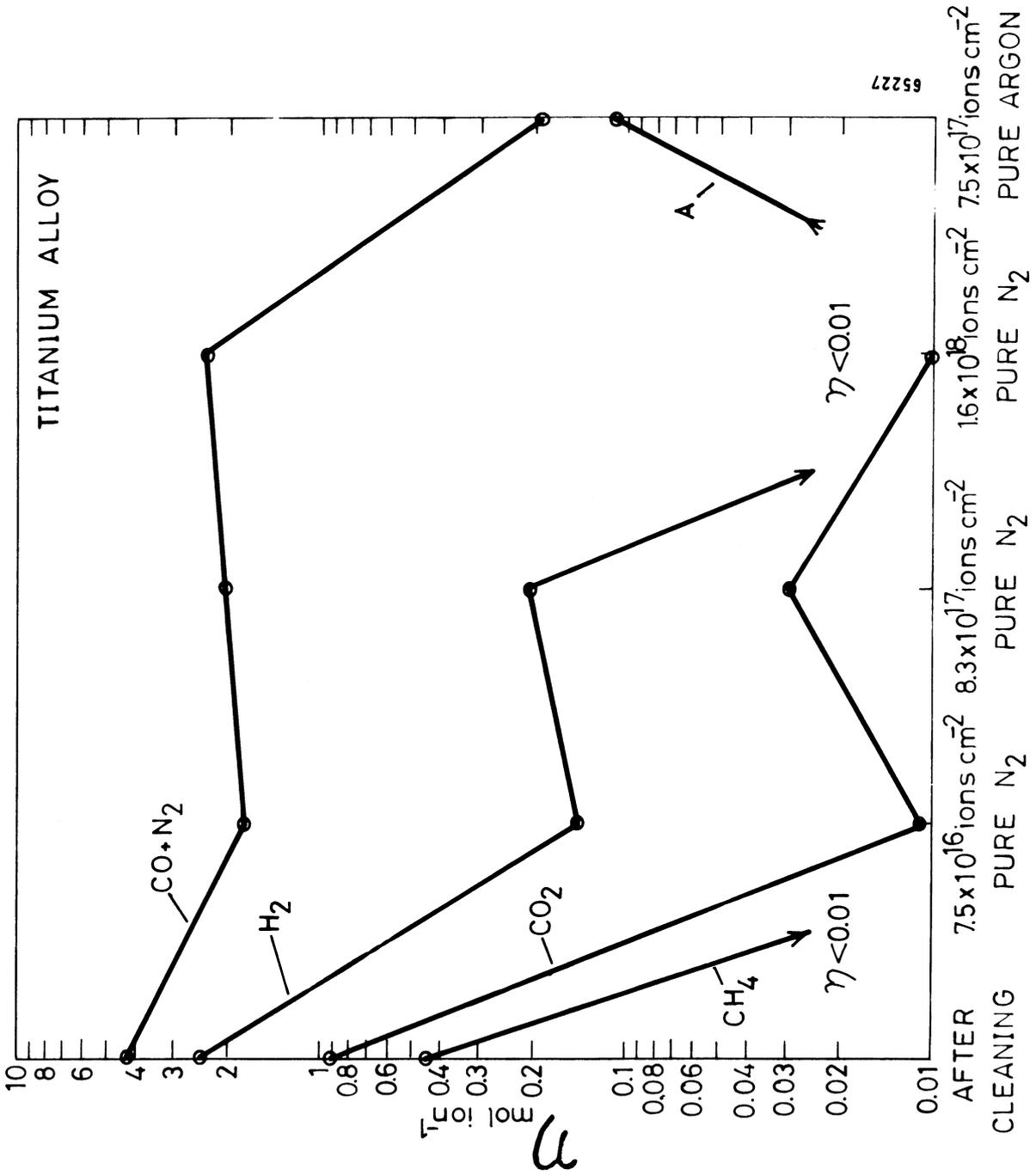
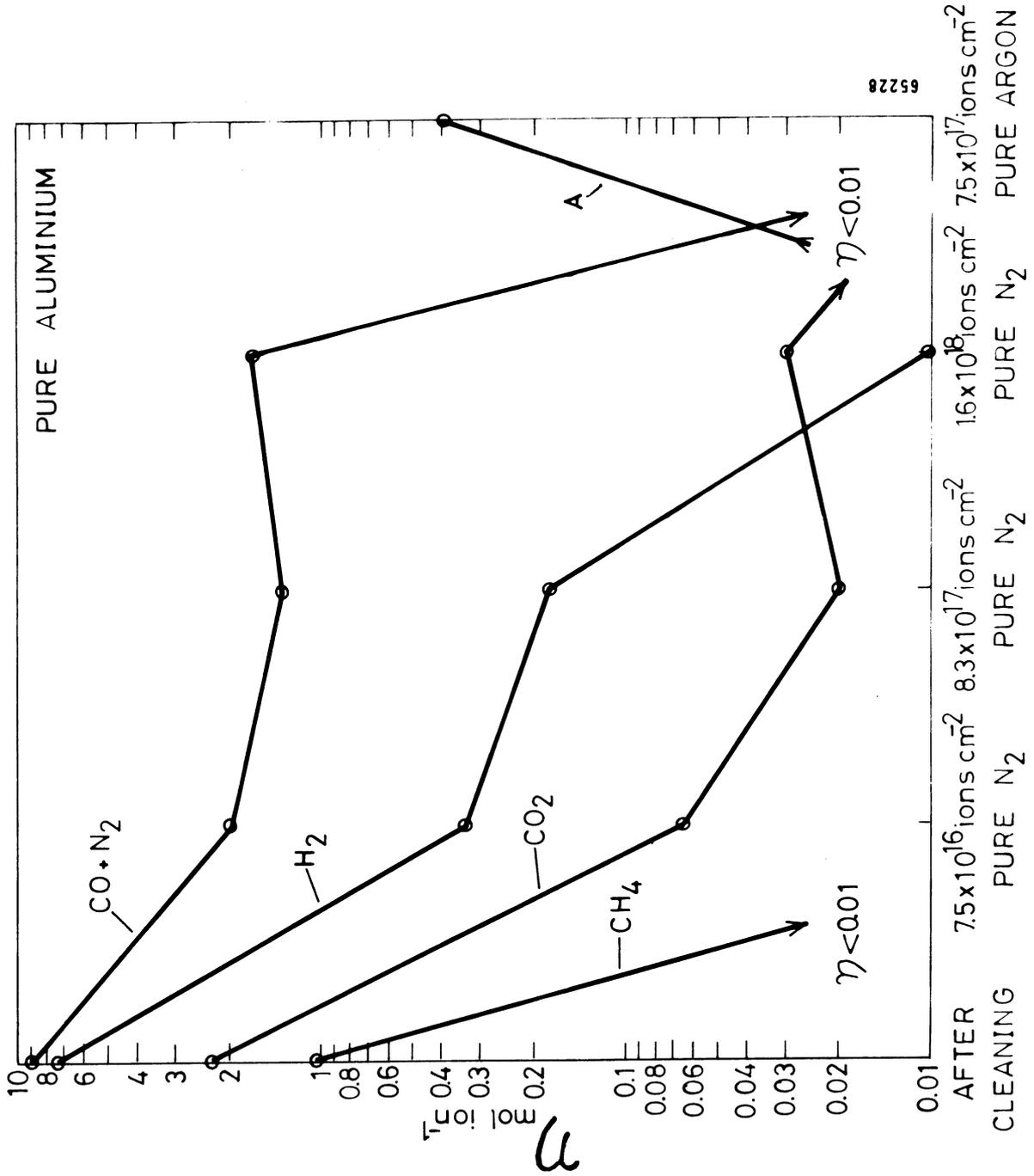


Figure 13



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Figure 14

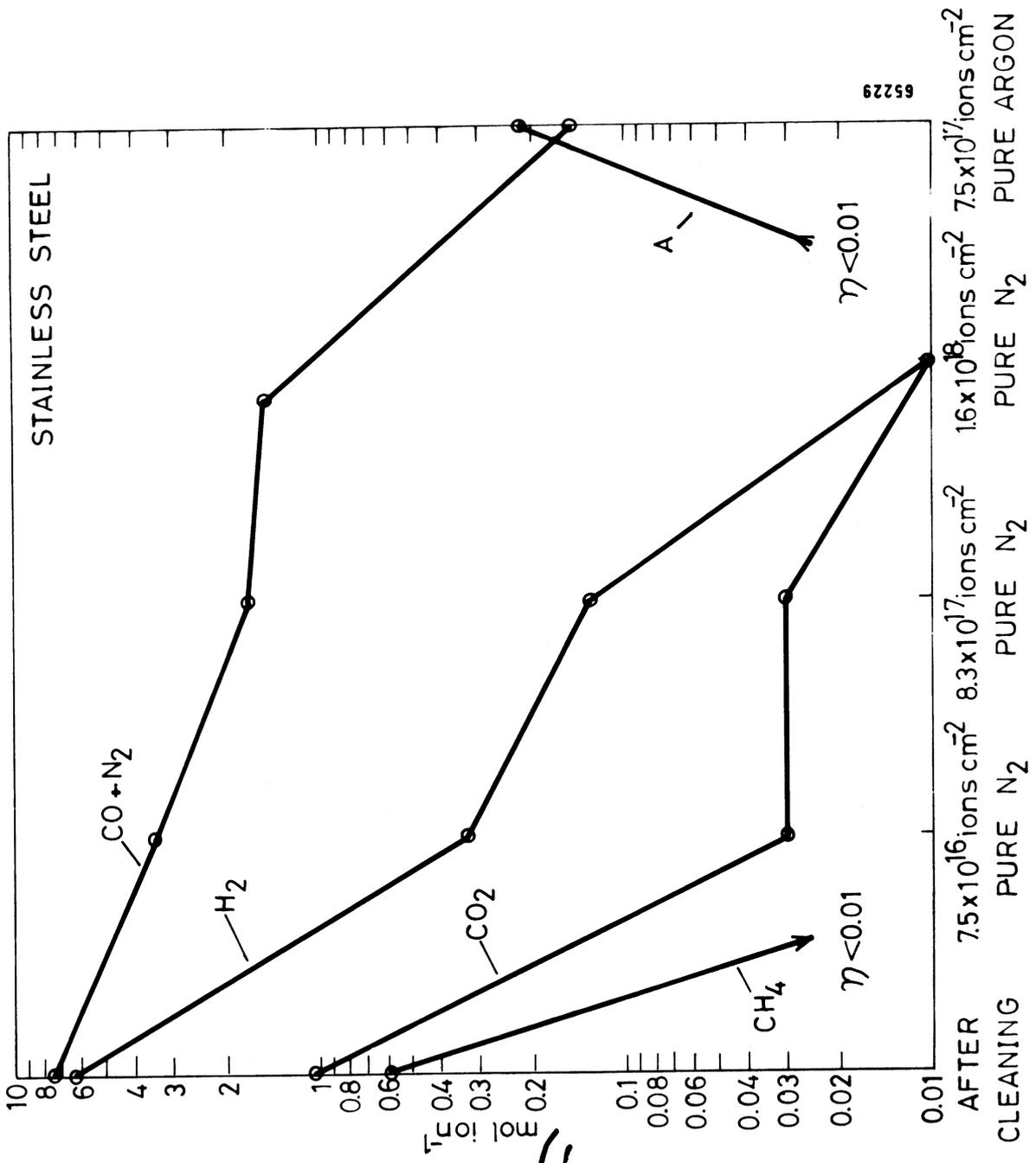


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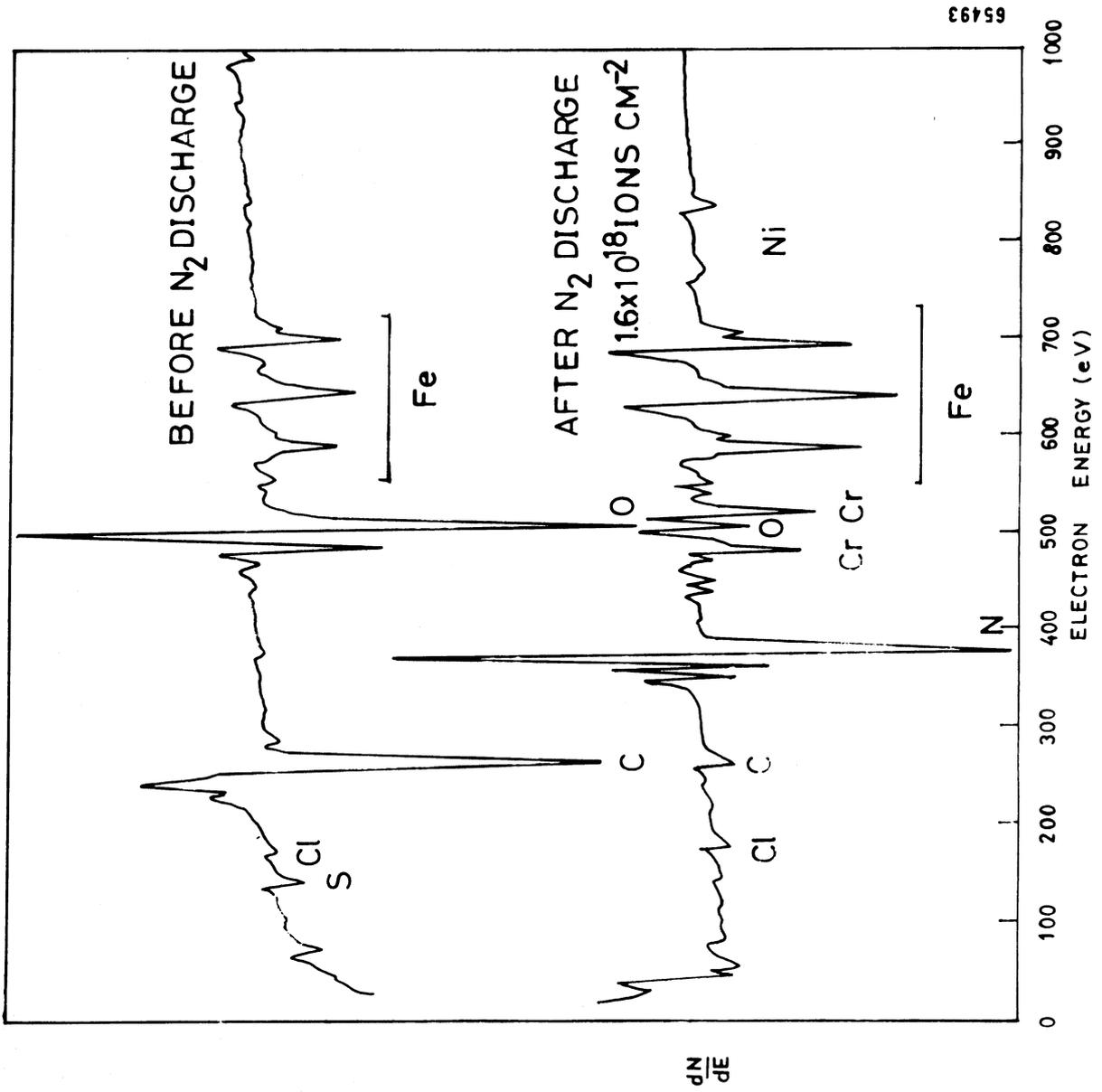


Figure 16

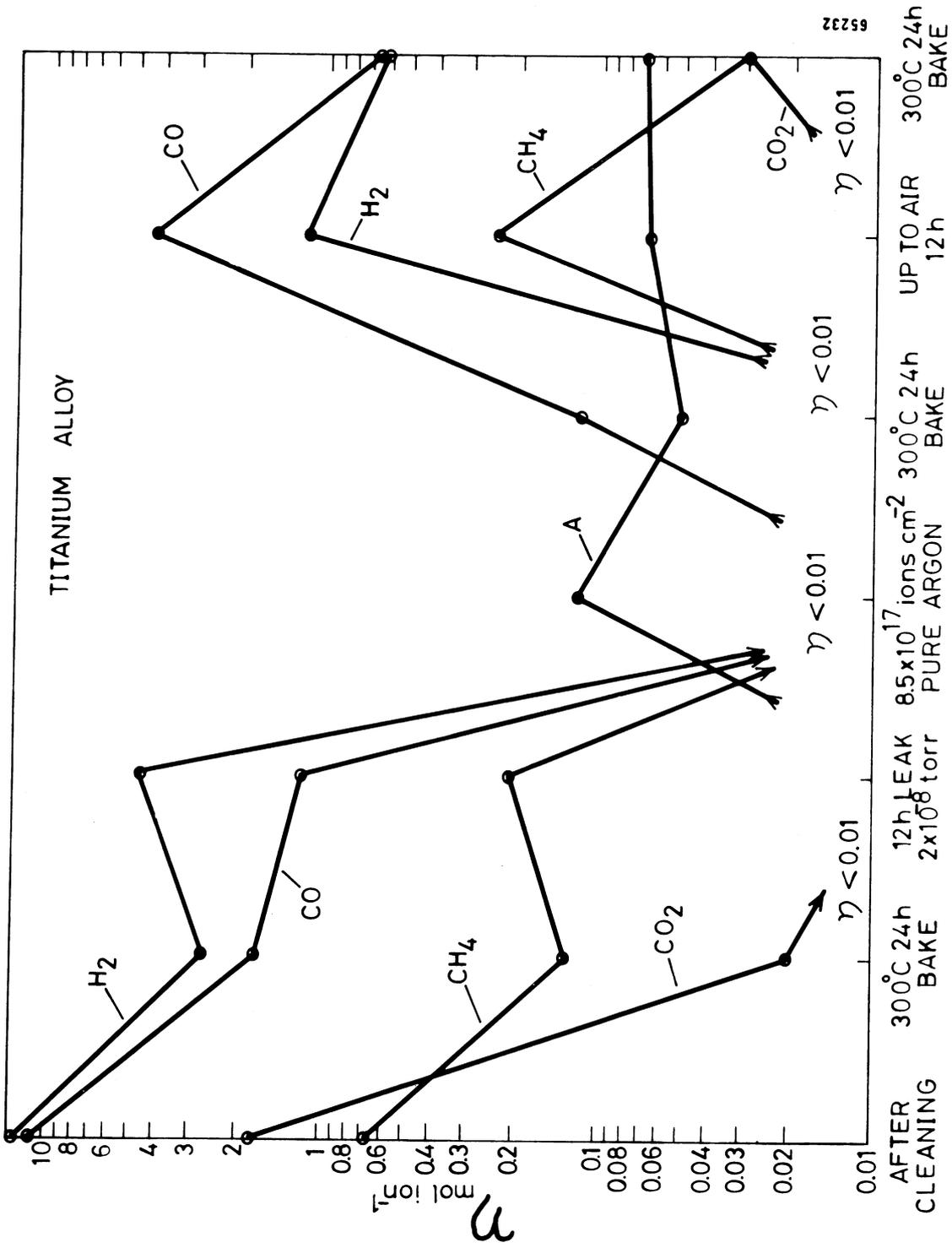


Figure 17

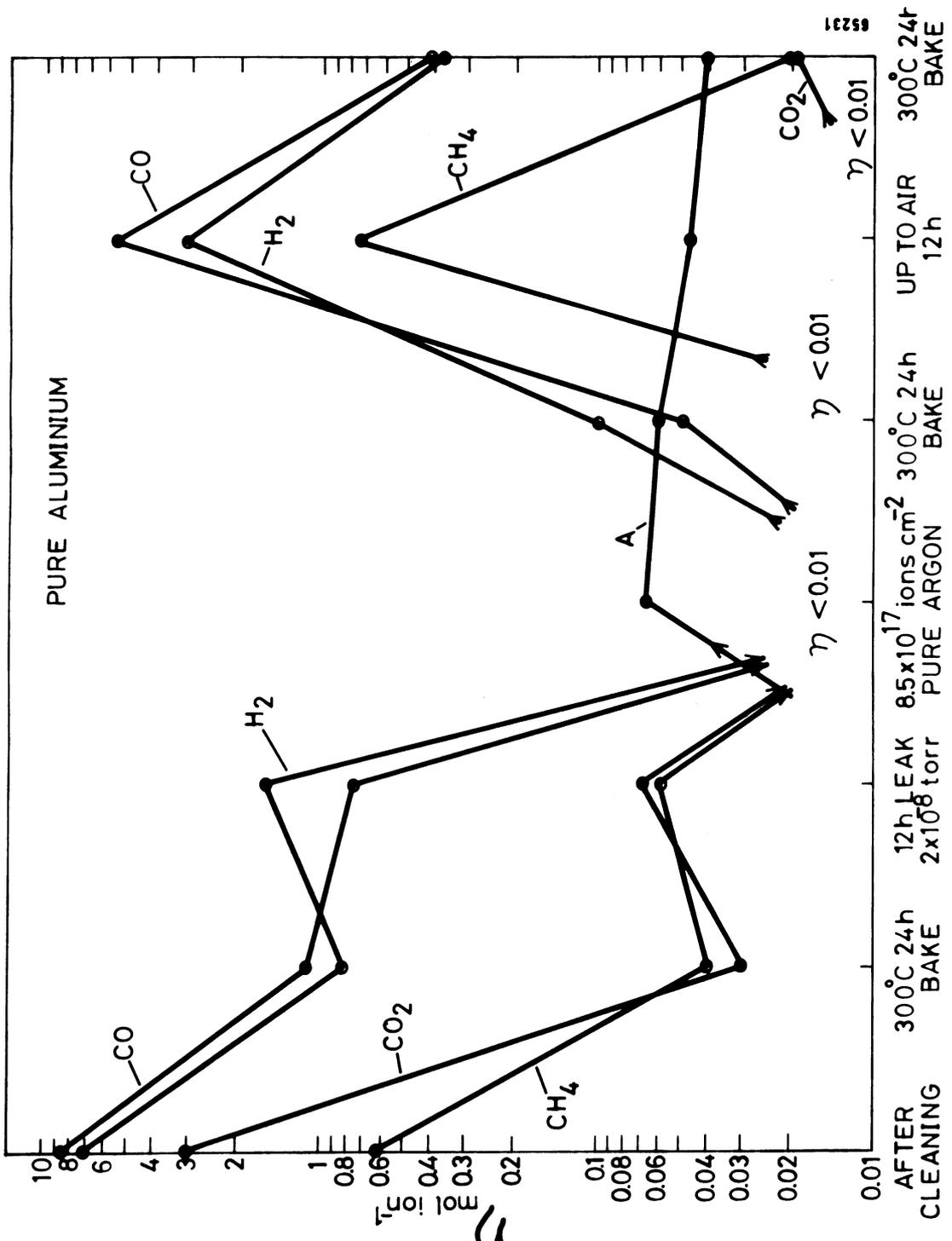


Figure 18

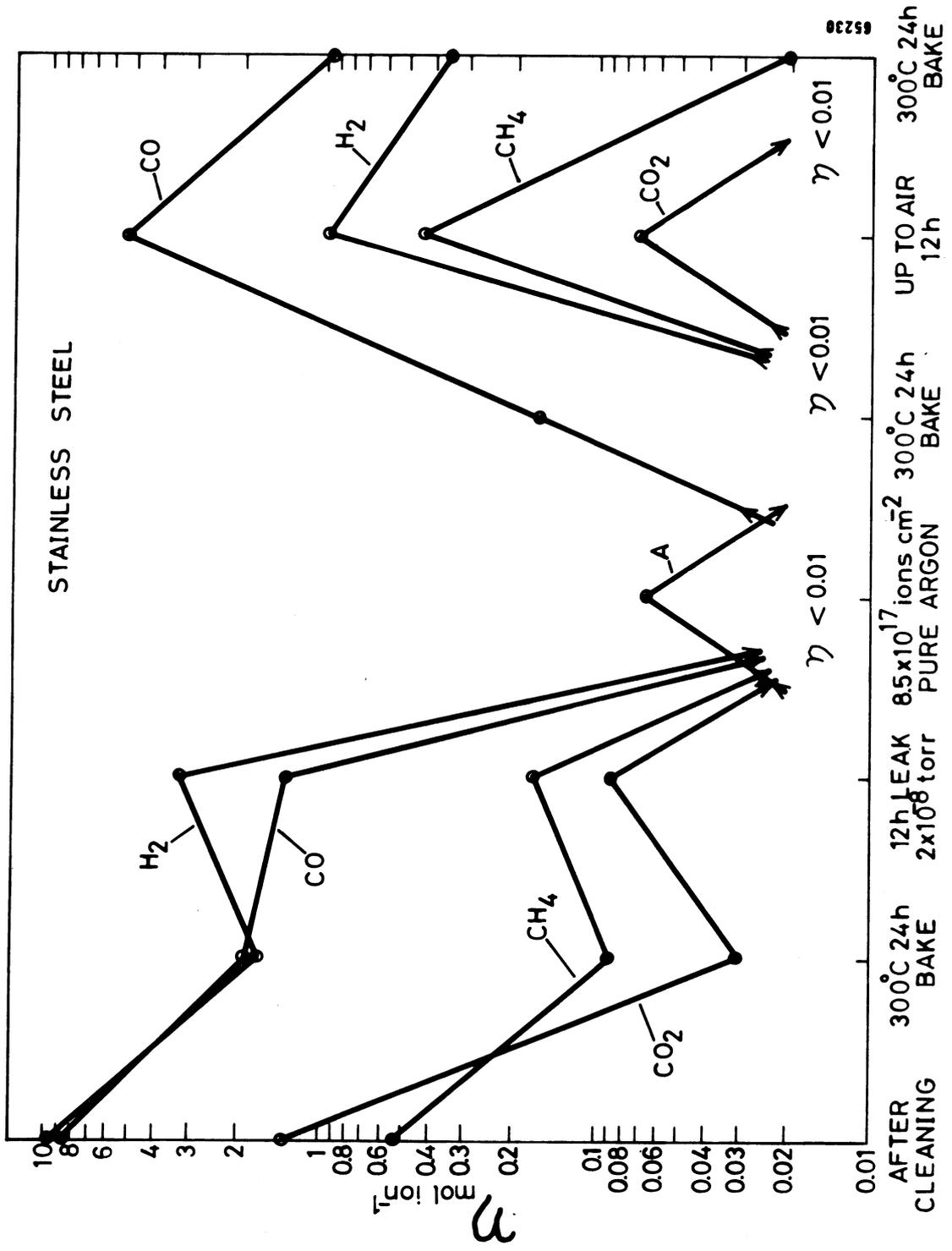


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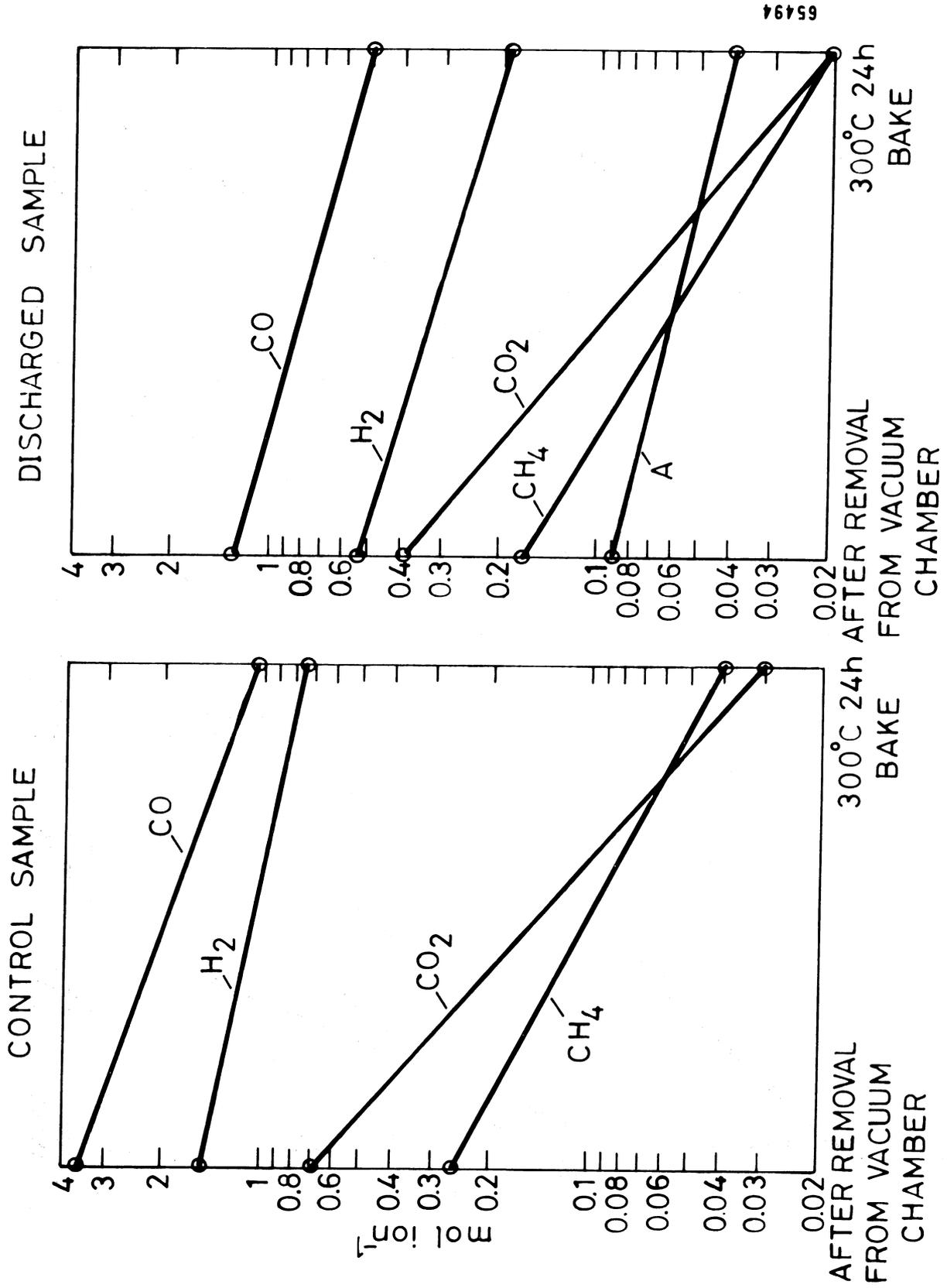


Figure 20

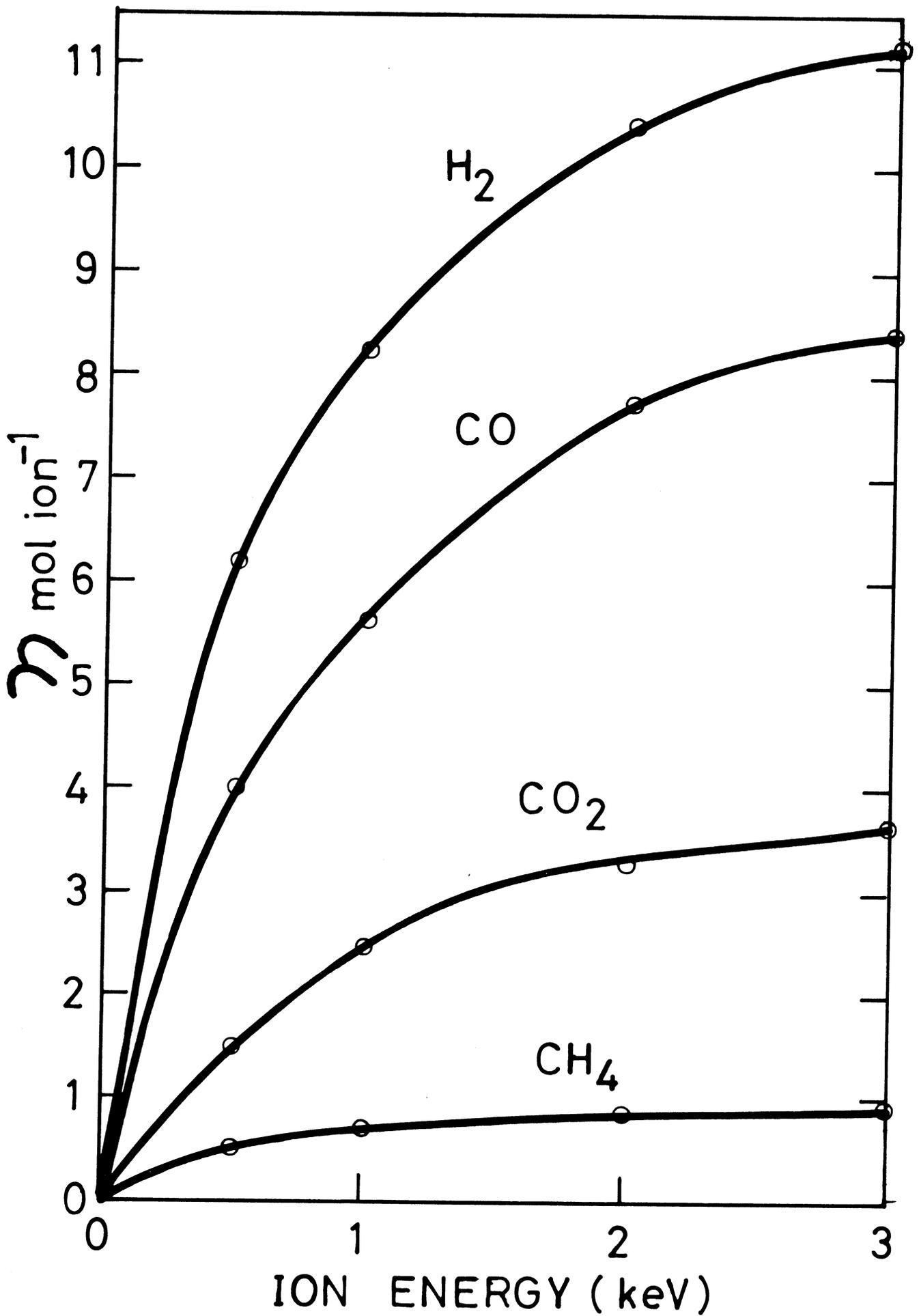


Figure 21