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## Outgassing Rates – An Introduction

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## OUTGASSING RATES - AN INTRODUCTION

R J ELSEY

This report is the text of a presentation at a meeting entitled IS GREEN CLEAN? organised by the Vacuum Group of the Institute of Physics, and held at the Society of Chemical Industry in London on the 24th February 1993.



# OUTGASSING RATES - AN INTRODUCTION

R J ELSEY

## PREFACE

Any restriction placed on our ability to clean materials for use in vacuum, including the metals from which chambers and components are manufactured, could result in a deterioration of the performance of the equipment including complete vacuum systems.

The method used up to now for monitoring the effect of pre-treatments on vacuum materials is the measurement of outgassing rates, which is the subject of this report. It deals briefly with the origins, effects and methods of reducing outgassing in vacuum systems. It then deals in detail with methods of measuring outgassing rates and ends with a discussion of results published by different authors.

Much of the report will be confined to a consideration of stainless steel which is widely used in high and ultra high vacuum technology and on which there is a considerable amount of published data.

## 1. OUTGASSING

Outgassing or more correctly thermal outgassing is the term used in vacuum technology to describe the slow evolution of gases from surfaces in a vacuum.

In the absence of leaks it is the main factor limiting the performance of vacuum systems by preventing the rapid attainment of a low pressure.

After the initial pumping of a system the pressure reduces slowly with time. Typically  $P$  the pressure is proportional to  $1/t$  where  $t$  is the pumping time.

Figure 1 is a typical outgassing rate diagram. It is usual to plot outgassing rates on logarithmic axes. The 45 slope demonstrates the  $1/t$  relationship.

If a vacuum system is heated and then held at a constant temperature as it is in an in-situ vacuum bake-out, the pressure rises to a peak, levels out and then slowly falls. When the system is cooled again to ambient temperature the pressure falls to a value considerably lower than it would have reached in the same time without the bake.

The residual gases in baked and unbaked systems are different. In an unbaked system the major gas present is water vapour. Of this the majority will have been adsorbed on the surface while the system was at atmospheric pressure.

In figure 1 the area under the curve represents the total quantity of gas removed from  $1 \text{ cm}^2$  of surface in 100 hours. Most of this will be water. The quantity in the figure, which is typical of e.g. mild steel would be sufficient to form 100 monolayers of water molecules on the surface.

Stainless steel would also adsorb several monolayers while exposed to atmospheric pressure. In an average vacuum chamber this could come from a few ppm of water vapour in the letting-up gas.

Metal surfaces are invariably covered with an oxide layer. This varies in thickness and porosity and may be more or less contaminated with carbon and other elements<sup>1</sup>. The type of oxide layer will depend inter alia on the pre-treatment to which the surface has been subjected i.e. the action of solvents, detergents and acid or alkali etchants.

Modern improvements in surface analysis help to characterise these effects but the microstructure does not always correlate with outgassing rates<sup>2</sup>. Much of the earlier work<sup>3</sup> was determined by trial and error.

The surface adsorbed gases can be removed by a modest in-situ vacuum bake at say 150 C. After such a bake the residual gas will be 90 - 100% hydrogen.

During production a small quantity of hydrogen ( less than  $1 \text{ mbar.litre/ cm}^3$  ) permeates the bulk of the metal. When under vacuum this will slowly diffuse from the surface and after the removal of surface gases will determine another limit to the low pressure that can be attained.

The outgassing rate will depend on the diffusion rate and the hydrogen concentration. Because they affect the ease with which hydrogen can be removed by baking the rate also depends indirectly on the thickness of the metal and the partial pressure of hydrogen outside the vacuum system.

The outgassing rate can be reduced by either reducing the diffusion rate or the hydrogen concentration in the metal.

The diffusion rate can be reduced by :-

- (a) reducing the operating temperature, e.g. as in a cold-bore super-conducting magnet;
- (b) using a different metal, e.g. aluminium<sup>4</sup>;
- (c) creating a barrier, e.g. a specially constructed oxide layer on the surface.

The hydrogen concentration can be reduced by :-

- (a) baking the vacuum system in-situ to a high temperature;
- (b) pre-baking the components in a vacuum furnace.

Calder and Lewin have calculated the baking conditions for stainless steel to reach a theoretical outgassing rate of  $10^{-16}$  mbar.l/sec/cm<sup>2</sup>. These are shown in table 1 for the case of 2mm thick stainless steel having an initial hydrogen concentration of 0.4 mbar.l/cm<sup>3</sup>. The table shows that the baking temperature must be at least 300°C or the baking time will be excessively long. Above 600°C the time is very short but for in-situ baking the temperature may be limited by problems of oxidation, strength and heat insulation, and by hydrogen permeating from the atmosphere outside.

Vacuum furnacing of the chamber and components before assembly to temperatures between 800 and 1000°C is very effective, especially as the improvement has been shown to be permanent<sup>6</sup>. After assembly of the furnaced components the system is baked to 150°C in-situ to remove surface gases. For such processing to be possible suitable furnaces must be available and the quality of the components has to be compatible with the high temperatures involved.

If the improvements are to be preserved great care must be exercised during packaging, transportation and assembly, also subsequent bakeouts must not be too high in temperature or long in duration or hydrogen will permeate back into the metal<sup>7</sup>.

## 2. MEASUREMENT OF OUTGASSING RATES

Four methods are available ; the collection, weight loss, pressure rise and throughput or dynamic flow methods.

### a) Collection Method

This method is of little practical importance. It consists of compressing the gas from the sample by means of a mercury diffusion pump into a small volume on the backing side.

The rate of pressure rise can be measured for example with a capacitor gauge. The method is not suitable for measuring very low outgassing rates and if a liquid nitrogen trap is used above the diffusion pump it will not detect condensable gases. It was used by Henry<sup>8</sup> for collecting samples of the outgassing gas for analysis.

## b) Weight Loss Method

The weight loss method consists essentially of weighing the sample with a sensitive balance, placing it for a given time in a high vacuum usually at an elevated temperature e.g. 50 or 100°C and re-weighing it. The result may be expressed in grams/hour/cm<sup>2</sup>.

The method is widely used for elastomers and synthetic resins in space and satellite technology and more details can be found in ESA and NASA documentation.

Some results have been published by Fulk and Horr<sup>9</sup>. It is possible to correlate these with those obtained by the pressure rise or throughput methods by assuming that the gas is predominately water vapour. It is not possible to find good agreement but the results are in the same area.

Podlaseck<sup>10</sup> has published details of a refinement of the method in which the balance is contained inside the vacuum and the sample is weighed continuously.

## c) Pressure Rise Method

Pressure rise tests are commonly used in vacuum practice for determining leakage or outgassing in vacuum systems. The procedure consists of isolating the system from the pump by means of a valve and timing the subsequent pressure rise.

For measuring outgassing rates the sample is placed in a leak-tight chamber of known volume or the sample may be

the chamber itself. See figure 2. Depending on the operating pressure range, the vacuum gauge may be a capacitor or ion gauge, or a mass-spectrometer.

$$\text{Outgassing rate } Q = \frac{VdP}{A\bar{d}t} \quad \text{where } A = \text{sample area}$$

It will be found that if the outgassing is due to surface desorption e.g. in the case of an unbaked metal, then the pressure will not rise linearly but will rise exponentially as desorption and re-adsorption eventually reach an equilibrium. In this case it is necessary to measure the pressure during the first few seconds or minutes after isolation and extrapolate to zero time. This can be done most easily using a recorder.

Account must be taken of any effects the gauge may have on the accumulating gas. It is well known that ion gauges and mass-spectrometers act as pumps and as sources of gas and can change the constitution of the gas.

If the method is used to measure the outgassing rate of hydrogen diffusing from the walls of a well baked system it has been found<sup>11</sup> that the pressure rise is linear up to pressures as high as  $10^{-1}$  mbar and periods of time as long as three months.

The method is particularly relevant to sealed-off devices or for example containers of pure gases.

A modification to the pressure rise method has been published by Yoshimura<sup>12</sup>. The difference is that the sample is contained in a small vessel separated by a

valve (  $C_2$  in figure 3 ) from the main pressure rise volume.

Pressure rise curves are constructed for the case when  $C_2$  is open and when it is closed. See figure 4.

$dP/dt$  values are determined for the same value  $P_r$  on the two curves.

In this way the effects of gauge pumping and outgassing from the empty vessel can be eliminated.

Yoshimura has used this method to measure outgassing rates for elastomers and ceramics and more recently<sup>13</sup> to evaluate different methods of treatment for stainless steel.

A variation of the pressure rise method was used by Elsey et al<sup>11</sup> to study the long term outgassing of sealed stainless steel and titanium volumes. These consisting of cylinders of  $150 \text{ cm}^3$  were first pumped and baked at  $120 \text{ C}$  for 16 hours, then isolated for periods of up to 3 months.

They were connected via a low conductance valve directly to the ion source of an MS10 mass-spectrometer. When the valve was opened the instantaneous pressure peak and the subsequent decay were recorded.

From the peak pressure, the decay constant and the estimated pumping speed at the mass-spectrometer the quantity of accumulated gas was determined.

#### d) Throughput or Dynamic Flow Method

This is the most widely used method and is particularly relevant to continuously pumped systems e.g. UHV systems.

The general principle of the method is shown in figure 5.

The sample vessel is connected via a low conductance  $C$  to a pump of speed  $S$  such that  $S \gg C$ .

Pressures  $P_1$  on the sample side and  $P_2$  on the pump side of the conductance are continuously measured.

At any time  $t$  after pumping commences:-

$$Q = \frac{(P_1 - P_2)C}{A} \text{ mbar.l/sec/cm}^2$$

The first published account of the method is by Zabel<sup>14</sup> of MIT in 1933. He used it for measuring vapour pressures of waxes and lacquers. These were coated on the inside of a glass tube which was connected to the pump by a length of narrow tubing which had a conductance  $C$  of 0.042 l/s. The gauge was an ionisation gauge.

It is more common for the apparatus to be constructed of stainless steel with the conductance  $C$  being a hole in a thin circular plate e.g. the apparatus used by Cross<sup>15</sup> and Grossart<sup>16</sup> to measure outgassing rates of epoxy-resin glass-fibre laminates used to make the vacuum chambers of the Nimrod particle accelerator.

To use the method for UHV it is necessary to either bake-out the whole apparatus every time a sample is changed or

to use a complicated system of vacuum locks and manipulators.

It is found that because pumps and gauges are working near their ultimate pressure that the pressures  $P_1$  and  $P_2$  approach each other, as do sample and blank runs. It is also found that outgassing from the ion gauge or mass-spectrometer can dominate that from the sample. Hence the trend towards large area samples<sup>17</sup>.

Moraw and Dobrozemsky<sup>18</sup> used a sample surface area of  $7,500\text{cm}^2$ . They also used low temperature thoriated iridium filament ion gauges (40 microamp emission) to minimise gauge effects. there was also a valve between the sample cylinder and the measuring apparatus to obviate the need for blank runs.

Moraw<sup>19</sup> in an earlier paper used a modified version of the same apparatus to determine the effects of the gauges and conductances on the outgassing results. The conductance could be switched between values of 0.1 and 1.5 l/s and an extra tungsten filament ion gauge was added to the system.

The sample was replaced by a leak valve for injecting known mixtures of gases.

Moraw showed that the thoriated iridium filament had less than half the pumping speed for hydrogen of the tungsten filament and had less effect on the other residual gases. He found that using the small conductance results were obtained that were a factor of 2 low and he recommends the use of a conductance of at least 3l/s for this area of sample.

Calder and Lewin<sup>5</sup> working at CERN in 1966 carried out an extensive investigation into the effects on outgassing of baking stainless steel.

Their apparatus figure 6 was , except for the sample cylinder and an all-metal valve, constructed of glass, including a quarter mm thick glass orifice plate with a conductance of 0.1 l/s and the two mercury diffusion pumps in series and the liquid nitrogen trap.

The same gauge, which in this case was an omegatron, was used to measure both  $P_1$  and  $P_2$  by means of glass ball and socket valves. The omegatron has few metal parts to outgas, has a very low pumping speed and also acts as a gas analyser.

Using this apparatus Calder and Lewin measured outgassing rates as low as  $10^{-14}$  mbar.l/sec/cm<sup>2</sup>.

Another variation which avoids the necessity of having two calibrated ion gauges is the Oatley<sup>20</sup> method which uses a number of different conductances<sup>21</sup> or a continuously variable conductance<sup>8</sup>.

To measure the outgassing rate  $P_1$  is measured for a number of different values of C. A graph is drawn of  $P_1$  against  $1/C$  (see figure 7) . The intercept on the  $P_1$  axis is then equal to  $P_2$  . Q is then determined in the usual way.

### 3. STAINLESS STEEL OUTGASSING RATES

Barton and Govier<sup>3</sup> studied the effect different surface treatments had on the room temperature outgassing rates of stainless steel. The results of their investigation are set out in table 2.

The bench mark by which they judged the others was honed to a fine finish (0.025 microns), vapour degreased, vacuum baked at 450°C, then exposed to air for 24 hours. This had an outgassing rate of  $8 \times 10^{-11}$  mbar.l/sec/cm<sup>2</sup> after 10 hours of pumping.

With regard to the other types of treatment they decided:-

- (1) the surface roughness made little difference;
- (2) vapour degreasing with trichorethylene left traces of the solvent even after 48 hours pumping;
- (3) vapour blasting with fine glass balls suspended in water with a detergent could remove stains and oxides from the surface without making the outgassing significantly worse;
- (4) electro-polishing made no improvement but did increase the level of hydrocarbons;  
(It is interesting that in a recent paper Yoshimura<sup>13</sup> found that electro-polishing made a factor of 50 improvement over mechanical polishing with a 10 hour rate of  $1.3 \times 10^{-11}$  mbar.l/sec/cm<sup>2</sup>.)
- (5) the Diversey process gave the highest rate ;  
(This agrees with the Strausser<sup>22</sup> results.)
- (6) air baking gave the best result similar to pre-baking in a vacuum furnace.

The outgassing rates in table 3 show the effect of in-situ baking to moderate temperatures.

With the exception of the results for air baking and the Yoshimura result for electro-polishing which are an order of magnitude lower these results are remarkably consistent regardless of the type of pre-treatment.

Finally table 4 presents results for traditionally baked UHV systems using temperatures of 300 to 400° C.

It shows how much more effective baking is for thin sheet than for thick, also the advantage of pre-treatment in a vacuum furnace at 800-1000° C.

The latter treatment was found to be permanent<sup>6</sup> and to survive a 5 month storage in air, after which it was possible by means of a 150° C in-situ bake to obtain outgassing rates in the  $10^{-14}$  mbar.l/sec/cm<sup>2</sup> range.

TABLE 1.

BAKEOUT TIMES OF 2MM THICK SHEET OF STAINLESS STEEL  
AT VARIOUS TEMPERATURES FOR  $Q = 10^{-16}$  mbar.l/sec/cm<sup>2</sup>  
HYDROGEN CONCENTRATION  $C_0 = 0.4$  mbar.l/cm<sup>3</sup>  
CALDER and LEWIN<sup>5</sup>

<u>TEMPERATURE</u>	<u>BAKEOUT TIME</u>
300° C	11 DAYS
420° C	24 HOURS
570° C	3 HOURS
635° C	1 HOUR

TABLE 2.

OUTGASSING RATES FOR UNBAKED STAINLESS STEEL

	<u>10 HOUR RATE X 10<sup>-10</sup></u> <u>mbar.l/sec/cm<sup>2</sup></u>
<u>BARTON and GOVIER</u> <sup>3</sup>	
MACHINED AND VAPOUR DEGREASED	1.3
HONED AND VAPOUR DEGREASED	1.6
GLASS BEAD BLASTED AND DEGREASED	2.7
ELECTRO-POLISHED	1.6
DIVERSEY DS-9 CHEM. POLISHED	2.9
VACUUM BAKED 450°C. 24 HOURS IN AIR	0.8
AIR BAKED 500°C	0.7
WIPED WITH CLEAN HANDS	1.3
<u>STRAUSSER</u> <sup>22</sup>	
VAPOUR DEGREASED	3.3
CHEMICALLY CLEANED	2.0
DIVERSEY DS-9 CHEM. POLISHED	4.4
<u>YOSHIMURA</u> <sup>13</sup>	
BELT POLISHED	7.0
BUFF POLISHED	4.0
ELECTRO-POLISHED	0.1

TABLE 3.

OUTGASSING RATES FOR MODERATELY BAKED STAINLESS STEEL

	<u>RATE AFTER COOLING X 10<sup>-12</sup></u> <u>mbar.l/sec/cm<sup>2</sup></u>
<u>STRAUSSER<sup>22</sup></u>	
VAPOUR DEGREASED, BAKED 150°C 24 HOURS	5.3
CHEMICALLY CLEANED, BAKED 150°C 24 HOURS	6.0
<u>YOUNG<sup>23</sup></u>	
GLASS BEAD BLASTED, BAKED 250°C 30 HOURS	2.7
ELECTRO-POLISHED, BAKED 250°C 30 HOURS	2.7
AIR BAKED 250°C 16 HRS, BAKED 250°C 15 HRS.	0.7
AIR BAKED 450°C 61 HRS. BAKED 250°C 15 HRS.	0.4
<u>MORAW and DOBROZEMSKY<sup>18</sup></u>	
DEGREASED IN ACETONE, VACUUM BAKED 150°C 20 HRS EXPOSED TO MOIST AIR FOR 30 MINUTES THEN :- VACUUM BAKED 100°C 20 HRS.	1.3*
AIR BAKED 100°C 2 HRS, VACUUM BAKED 100°C 18 HRS	0.13*
AIR BAKED 400°C 2 HRS, VACUUM BAKED 400°C 18 HRS	0.05*
* Nitrogen equivalent	
<u>YOSHIMURA<sup>13</sup></u>	
BELT OR BUFF POLISHED, VACUUM BAKED 200°C	20.0
ELECTRO-POLISHED, VACUUM BAKED 100°C	2.0
ELECTRO-POLISHED, VACUUM BAKED 150°C	0.1
<u>BENNETT and ELSEY<sup>17</sup></u>	
VACUUM BAKED 150°C 10 DAYS	0.3
AIR BAKED 200°C 24 HRS, VACUUM BAKED 150°C 10 DAYS	0.1

TABLE 4.

OUTGASSING RATES FOR BAKED STAINLESS STEEL

RATE AFTER COOLING X 10<sup>-14</sup>  
mbar.l/sec/cm<sup>2</sup>

CALDER and LEWIN<sup>5</sup>

2mm thick sheet

VACUUM BAKED AT 300°C FOR 25 HOURS	520
" " " 300°C " 100 "	147
" " " 360°C " 45 "	288

0.25 mm coiled strip

VACUUM BAKED AT 360°C FOR 24 HOURS	3.1
VACUUM BAKED AT 1000°C FOR 3 HOURS IN FURNACE FOLLOWED BY 360°C FOR 24 HOURS IN-SITU	1.6

YOUNG<sup>23</sup>

3mm thick sheet

VACUUM BAKED AT 250°C FOR 30 HRS + 450°C FOR 17 HRS	53
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NUVOLONE<sup>5</sup>

vapour degreased and Diversey 708 cleaned then :-

VACUUM BAKED AT 300°C FOR 40 HOURS	642
VACUUM BAKED AT 800°C FOR 2 HRS. IN FURNACE FOLLOWED BY 150°C FOR 20 HRS IN-SITU	35
BAKED AT 400°C IN 27 mbar O <sub>2</sub> FOLLOWED BY VACUUM BAKE AT 150°C FOR 20 HRS IN-SITU	21

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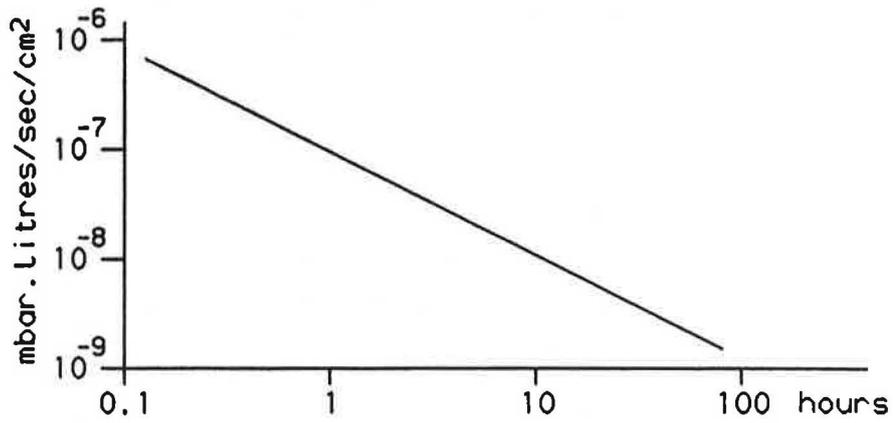


Fig 1 Graph of typical outgassing rate

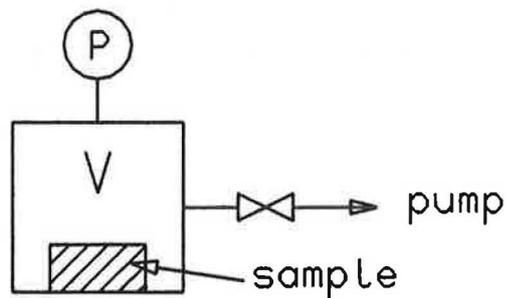


Fig 2 Schematic of pressure rise method

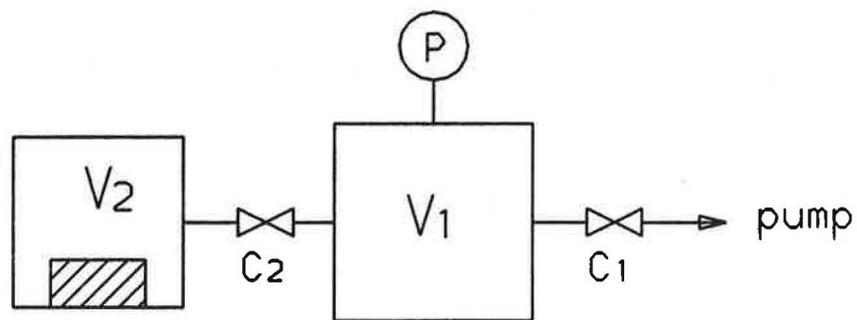


Fig 3 Yoshimura variation of pressure rise method

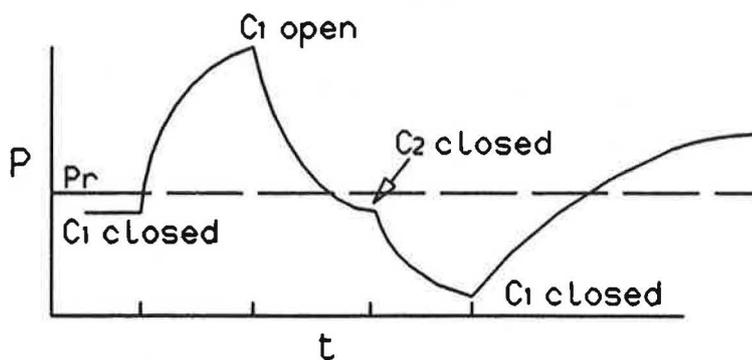


Fig 4 Pressure rise diagram from Yoshimura method

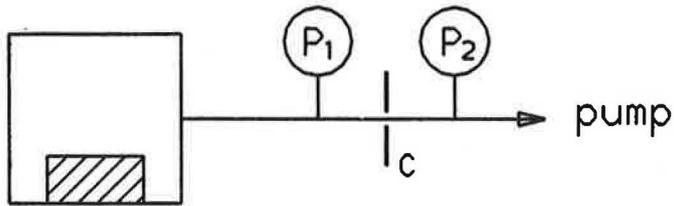


Fig 5 Schematic of throughput method

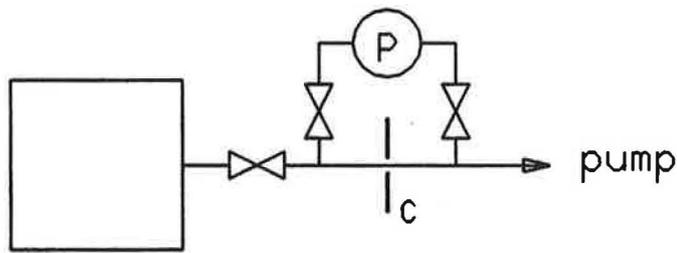


Fig 6 Calder and Lewin variation of throughput method

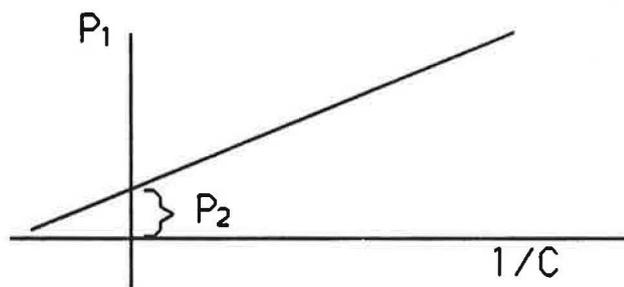


Fig 7 Use of variable conductance to obtain  $P_2$







