Outgassing rates from stainless steel and the effects of gauges

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Outgassing rates from stainless steel and the effects of gauges

With additional material to that presented at IVC-8, Berlin, June 2003, published in Vacuum, 73 (2004) 149-153, giving the rate of production of methane by the gauge.

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Abstract

The outgassing of stainless steel has been measured taking account of the production in the measuring gauge. Production of carbon monoxide and carbon dioxide in the gauges is shown to contribute at least 80% of the measured partial pressures. By using an isolation pressure rise technique coupled to NEG pumping it is possible to measure the outgassing of methane at very low levels. The specific outgassing rate of methane from 304L stainless steel is found to be $\leq 5 \times 10^{-22}$ mbar l s^{-1} cm^{-2}. It is concluded that only hydrogen and water outgas from clean stainless steel, but the water behaves strangely and may be created continuously on the surfaces of the steel. The rate of production and break-up of methane by the action of the gauge is also measured.

Keywords: Vacuum; Outgassing rate; Hydrogen; Methane; Carbon monoxide; Carbon dioxide; Water; Stainless steel; Quadrupole mass analyser; NEG pump

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1. Introduction

It is well known that hot filaments and plasmas act as "chemical factories" in vacuum systems to produce certain gases – mainly water, carbon monoxide, carbon dioxide and methane. Thus, ion, Penning and magnetron gauges, ion sources, including those in quadrupole mass analysers (QMA), and ion pumps produce these gases. It is thought that the production is due to hydrogen and oxygen reacting with the carbon on the surfaces. Summaries of these effects are to be found in references [1,2], which also give more references for further reading. Dylla and Blanchard [3] report on the problem with ion sources in mass spectroscopy at relatively high pressures for fusion plasma diagnostics.

Several authors report outgassing of methane, see for example [4-11]. However, investigations [12,13] showed that most, if not all, of the methane from stainless steel was produced in the ion source of the measuring equipment. The real specific outgassing rate was measured to be $\leq 2 \times 10^{-17}$ mbar l s^{-1} cm^{-2}. The problem is apparent at low outgassing rates where accurate measurement is most difficult. In certain situations it is important to have very low partial pressures of hydrocarbons and it is vital to know if methane is really outgassing from the surfaces or is being manufactured in the gauges. In the latter case, turning off the gauges will solve the problem but at the cost of not knowing the pressure. (A gauge, operating at uhv pressures, that does not rely on ionisation is not easy to find!) This experiment was designed to extend the previous measurement [12,13] of the real outgassing of methane from stainless steel. Hydrocarbons heavier than methane have not been observed in the mass spectra. In addition the outgassing of carbon monoxide, carbon dioxide and water was investigated.

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While most partial pressures of methane are only a small fraction of the total (mainly hydrogen) in pumped uhv systems, it is interesting to note the measurements of Klopfer et al [4] on sealed-off getter pumped vacuum tubes containing hot cathodes. In this case, the methane was predominant because the getters do not pump the methane.

2. The Isolation Pressure Rise Technique

The isolation pressure rise technique (IPR) is useful to measure outgassing rates. A vessel of volume V, containing the material to be measured, of surface area A, is pumped down and isolated. The pressure rise of the constituent gases Δp, in a given time t is then measured and the outgassing rate is given by,

$$g = \frac{V\Delta p}{At} \tag{1}$$

To overcome the problem of the manufacture of methane in the measuring gauge, a feature of the non-evaporable getter pump was used; the NEG does not pump methane. The IPR chamber was continuously pumped after closure so that the only pressure rise was due to gases not pumped by the NEG (hydrocarbons and noble gases). After a long time the system was opened up and the pressure rise of the residual gases monitored on an external quadrupole mass analyser. Figure 1 shows the system, which is built of all metal and ceramic components to uhv standards. The original measurements had been made on a large chamber [12], but to increase the sensitivity in the present experiment the chamber volume is small but the surface area is relatively large. In addition, the IPR is over a longer time, again to increase the sensitivity.
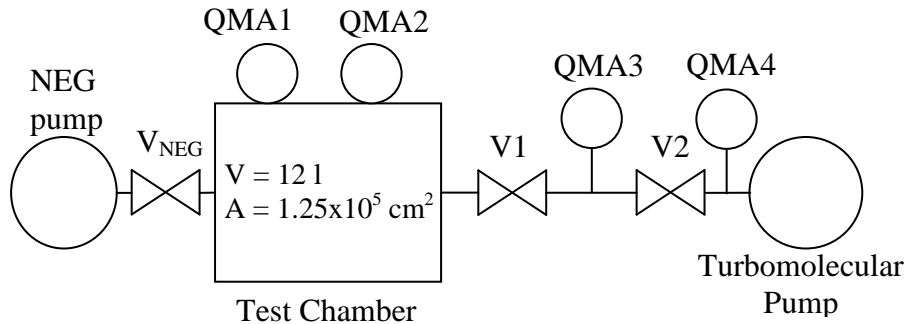

Figure 1. Schematic diagram of the vacuum system.

The chamber is built from 304L stainless steel and has a volume of ~12 l, excluding the contents but including the NEG and up to valve V1. The volume between V1 and V2 is 0.7 l. The chamber holds 250 sheets of 0.5 mm thick 304L stainless steel sheets which have a total surface area of 1.25×10^5 cm^2.

The empty system (but not the QMAs, the NEG pump or the stainless steel sheets) was initially baked in air at 200°C for 1 day. The gauges, NEG and the sheets were added and the system was pumped by the 330 l/s turbomolecular pump. After reaching a pressure of ~10^{-6} mbar the system was baked at 150°C for 10 days to remove most of the water. The NEG was also activated during this period. This relatively low temperature baking scheme was developed for a proposed interferometric gravity wave detector [12]. The system reached a pressure of approximately 4×10^{-11} mbar. The stainless steel sheet had undergone the air bake some 10 years previously. One of the interesting measurements was to see if the beneficial effects of the air bake on reducing the outgassing rate (previously measured at 3×10^{-13} mbar l s^{-1} cm^{-2} [12]) were still retained after the sheets had been left in atmosphere (wrapped in aluminium foil) for this length of time.

Four nominally identical quadrupole mass analysers[*] (double filter analysis, mass 1-100 amu, dual Faraday cup/secondary electron multiplier detectors) were attached to the system, as shown in Figure 1. All had tungsten filaments in the uhv miniaturised ion sources with platinum source cages. The system can read down to pressures of ~5×10^{-14} Torr. The QMAs were attached to a PC for control and monitoring. The system reads in Torr and this report gives all direct measurements in Torr. Conversions into nitrogen equivalent pressures with the appropriate calibration are given in mbar.

The chamber was isolated by closing valve V1; the valve V_{NEG} remained open to pump the test chamber of all but the hydrocarbons and noble gases. Quadrupoles QMA1 and QMA2 were off but QMA3 and QMA4 remained on and were pumped by the turbomolecular pump. After 3.8×10^7 s (440 days), V2 was closed and V1 immediately opened. The pressures of various residual gas species were recorded on the QMA3 and are shown in Figure 2.
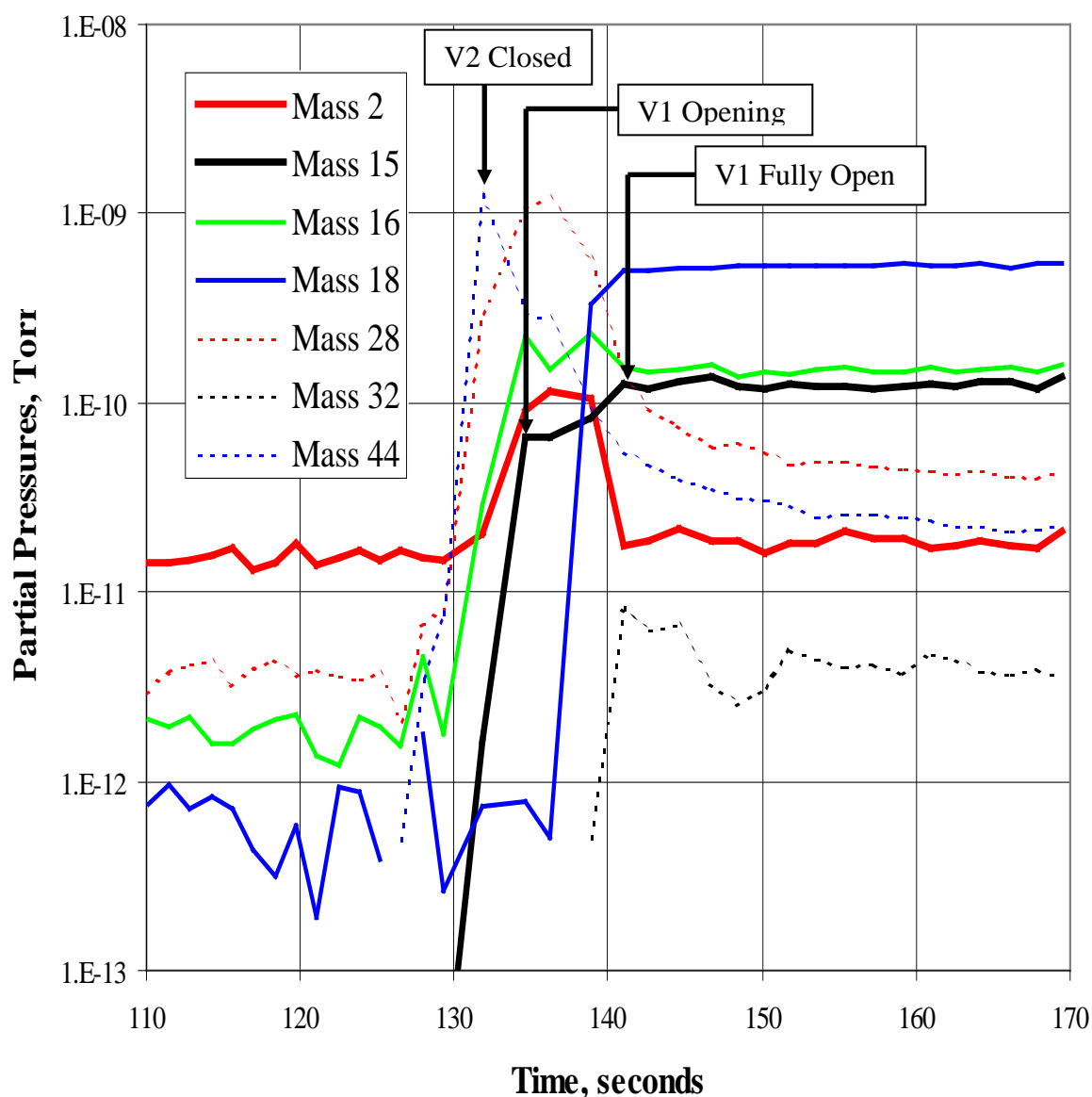

Figure 2. QMA3 readings at the end of the long IPR. The plots of the different masses are slightly offset (up to ~1 s) in time.

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[*] Spectra Windows Satellite 100, from Leda-Mass Ltd, now MKS Spectra, Crewe, CW1 6AG, UK.

3. Measurements
3.1 The long IPR to show methane is not outgassed from SS.

Figure 2 shows the mass spectral peaks of a number of masses as the valve V2 is closed and V1 is opened. The plot covers only 60 s. The closure of V2 is marked by a rise in the pressures, since the gauge is not now pumped. The opening of V1 is marked by a further discontinuity in the pressure, in many cases a lowering of the pressure.

To measure the methane, mass 15, rather than the major peak at 16, is used to avoid any confusion with oxygen, at mass 16, which is mainly from water. It can be seen that the mass 15 peak increases from below 10^{-13} Torr and rises to ~8×10^{-11} Torr as V2 is closed. When V1 starts to open the pressure rises more slowly due to the fall in the hydrogen pressure in the gauge (due to the NEG pumping) and sharing the methane between the much larger volume of the test chamber and the small volume between V1 and V2. With V1 fully open the 15 peak rises more slowly with time.

The change in the methane pressure, as recorded by mass 15, from closing V2 and fully opening V1 is 4×10^{-11} Torr (before corrections and calibration has been added). It can be argued that during the ~2 seconds required to fully open V1, the mass 15 peak would have risen to ~10^{-7} Torr if it had carried on rising at the same rate on closing V2. This quantity of gas in the volume between V1 and V2 when shared with the test volume could easily account for the pressure at the point where V1 is fully open. Hence the methane accumulated in the test volume during the IPR is probably close to zero or certainly less than 10^{-11} Torr. At worst ignoring all the evidence, the mass 15 peak could not have risen to more than 1.4×10^{-10} Torr, which is the final pressure on fully opening V1.

3.2 Rates of production and break-up of methane by the gauge

Figure 3 shows the peak heights of masses 2, 12, 14, 15, 16, as a function of time from the start of an IPR of the test volume (V1 closed, NEG on, QMA1 on). Other masses are omitted to avoid confusion and are less than 1×10^{-11} mbar. The NEG pump maintains the pressure of all the gases except for the methane.
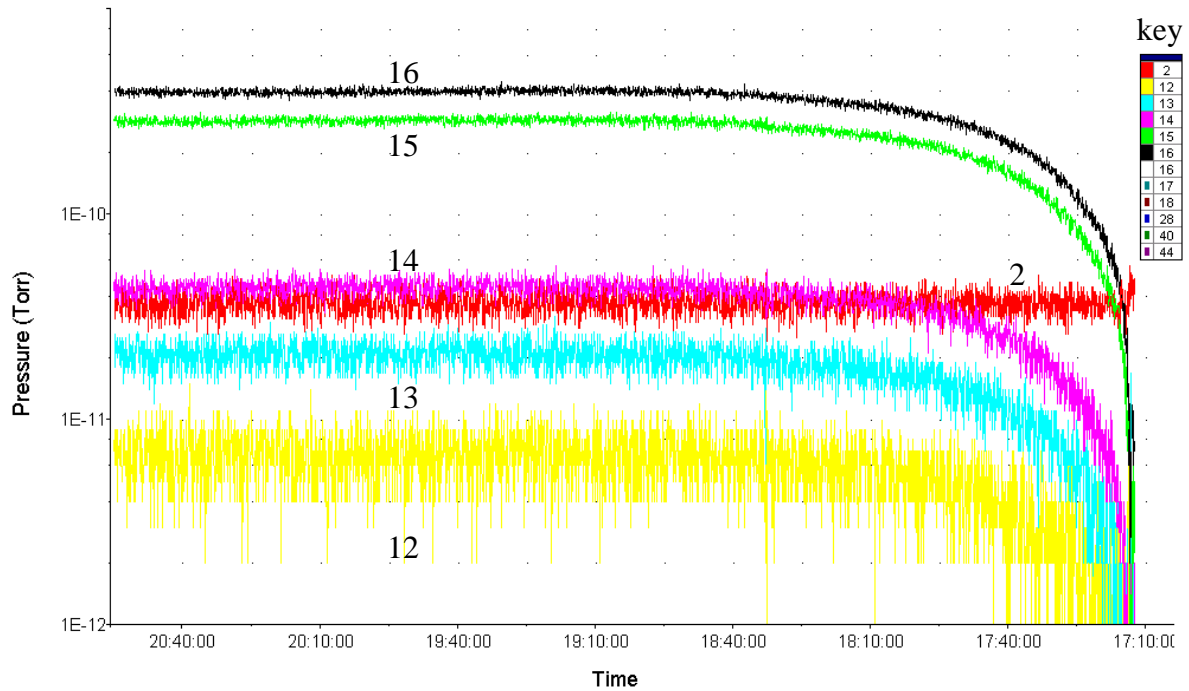

Figure 3. IPR of the test chamber with QMA1 on, NEG pump on, V1 closed. Only masses 2, 12, 13, 14 and 15 are shown to avoid confusion. Note that the time, in hours minutes and seconds, goes from right to left.

The peaks of masses 12, 14, 15 and 16 are in the ratio 2, 5, 11, 74, 100, respectively. The Mass Spectra Data Centre [14] gives the ratios as: 1, 3-9, 8-17, 75-86, 100, depending on the instrument and the way it is set up. The manufacturer of the gauge used gives values of 9, 16, 86, 100 for masses 13, 14, 15, 16. The present measurements are in reasonable agreement with these figures.

The methane peaks appear to rise up exponentially with time and then flatten out. A steady production rate would not produce this type of curve. Previous experiments [12] had found that the methane pressure was linked to the hydrogen pressure. Assume that the rate of production is proportional to the hydrogen pressure, H, then,

$$\frac{dp}{dt} = \alpha H \tag{2}$$

$$p = \alpha H t$$

There is presumably an equilibrium set up between formation and break-up of the methane The rate of formation of methane can be expressed by,

$$\frac{dp}{dt} = \alpha H - \beta p \tag{3}$$

where the second term is the rate of break-up of methane, assumed to be proportional to the methane pressure. The solution is,

$$p = \frac{\alpha H}{\beta} \left(1 - e^{-at}\right) \tag{4}$$

Measurements of the methane during a short IPR of the volume between valves V1 and V2, with QMA3 on, indicated that the methane (mass 15 peak) did not level off but continued to rise at the same rate as the hydrogen. (This volume is not pumped and the partial pressures of hydrogen, water and other gases rise.) Figure 4 shows the peak heights of masses 2, and 15 as a function of time.
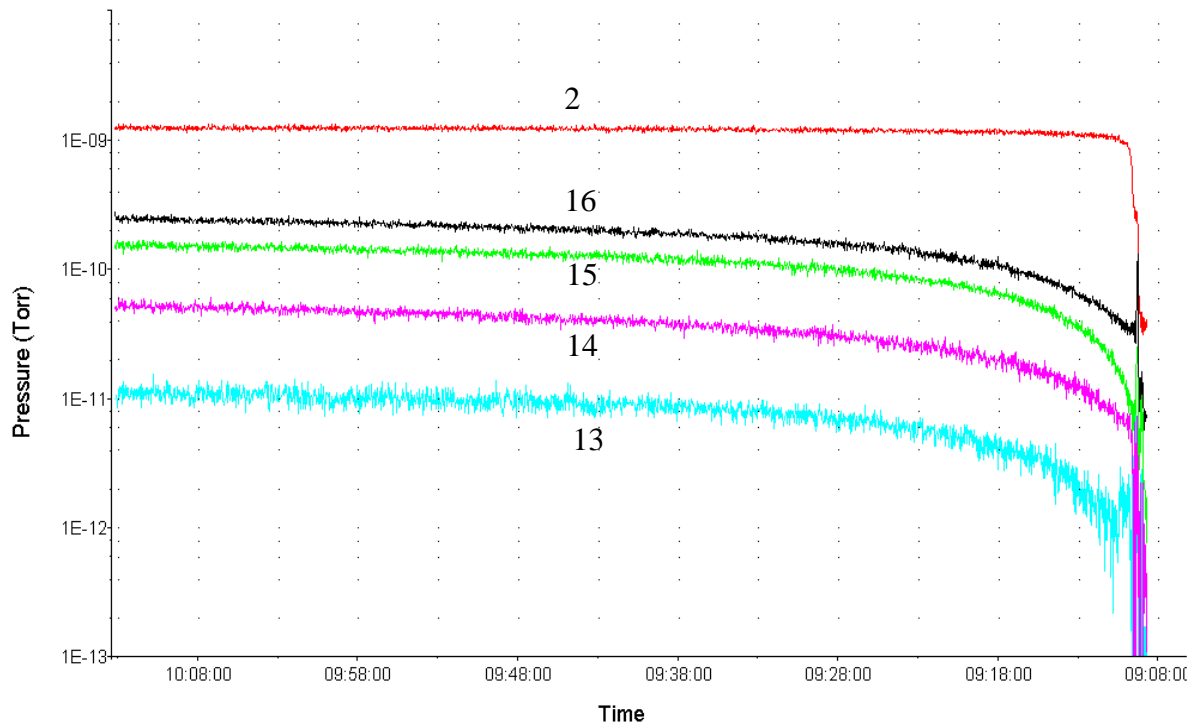

Figure 4. IPR of the volume between valves V1 and V2, with the QMA1 on, V1 closed and V_2 closed. Only masses 16,15, 14, 13 and 2 shown. Note that the time, in hours minutes and seconds, goes from right to left.

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On closing off the system to all pumping the hydrogen pressure is seen to rise rapidly to 10^{-9} Torr and then rise very slowly. It is assumed that the QMA pumps the system at a low rate which produces the almost constant pressure. It is not clear why the pressure should rise slowly after reaching the partial equilibrium. If the initial rise in hydrogen pressure is ignored and the pressure is assumed to rise linearly with time for the whole of the IPR then it is simple to calculate the effect on the methane production rate assuming that it is proportional to the hydrogen pressure.

Assuming a linear rise in hydrogen pressure with time,

$$H(t) = H(1 + \gamma t) \tag{5}$$

equation 3 becomes,

$$\frac{dp}{dt} = \alpha H(1 + \gamma t) - \beta p \tag{6}$$

The solution is,

$$p = \frac{\alpha H}{\beta}\left[\left(1 - \frac{\gamma}{\beta}\right)\left(1 - e^{-\beta t}\right) - \gamma t\right] \tag{7}$$

4. Calibration

A quadrupole mass spectrometer is not ideal to measure pressures. The gauge reads peak heights and not the partial pressure. The peaks can be shaped in width and amplitude by adjusting the resolution and mass offset voltage setting on the analyser and the amplitude altered by the voltage on the multiplier.

It was decided to calibrate QMA3 with a standard helium leak of 2×10^{-7} mbar l s^{-1}. The speed of the turbomolecular pump and the conductance of the pipeline between the gauge and the pump (from the dimensions) were known. The resultant speed at the gauge was calculated to be $S = 5.1$ l s^{-1} for helium. The peak reading of the QMA was compared to the calculated pressure, $P = Q/S$. The sensitivity of the analyser to helium was included in the calculation. The QMA peak height gave a nitrogen equivalent reading of 5.7×10^{-8} mbar compared to the calibration of 3.9×10^{-8} mbar. Thus the QMA peak height overestimates the reading of helium partial pressure by a factor of 1.48. All the QMAs were set up to have approximately the same sensitivity on all masses.

This calibration factor was used to estimate the partial pressure of the methane. Methane has a gauge sensitivity of 1.6 relative to nitrogen, so finally the peak heights of the methane peaks must be multiplied by 0.925 to get the true nitrogen equivalent pressures. Since mass 15 was used for the methane measurement the peak height of this mass must be corrected by the relevant cracking pattern. Using the figures for the peak heights given by the gauge manufacturer, the peak height of mass 15 is 41% of the total. Hence, the peak height of mass 15 is multiplied by $0.925/0.41 = 2.27$ to obtain the nitrogen equivalent partial pressure of methane.

5. Results
5.1 Methane

The measured change in pressure of mass 15 on opening valve V1 is 4×10^{-11} Torr. Multiplying this by the calibration factor obtained in the section above provides the partial pressure of methane accumulated over the IPR of 14 months as 1.1×10^{-10} mbar. Putting this number into (1) gives the specific outgassing rate of methane as, $g = 2.9\times10^{-22}$ mbar l s^{-1} cm^{-2}. The outgassing rate is probably an overestimate since there is strong evidence, as explained in section 3, that there was no, or very little, accumulated methane. The accuracy of the calibrating leak is ±10% and of the measurement is estimated to be ±30%. Thus the outgassing rate is in the range 0–5×10^{-22} mbar l s^{-1} cm^{-2}.

Whilst the evidence shows that the gauges produce the methane, the measurements of the IPRs described in section 3.2 give the rates of production and break-up by the gauge over widely different pressure of hydrogen in the system. The pressure rise of methane (mass 15) found by fitting (4) to the data shown in Figure 3 give the rate constants as: $\alpha = 4\text{x}10^{-3}$ s^{-1} and $\beta = 5.2\text{x}10^{-4}$ s^{-1} ($H = 3.75\text{x}10^{-11}$ Torr, uncorrected QMA reading). The fit to the data is very good, see Figure 5.
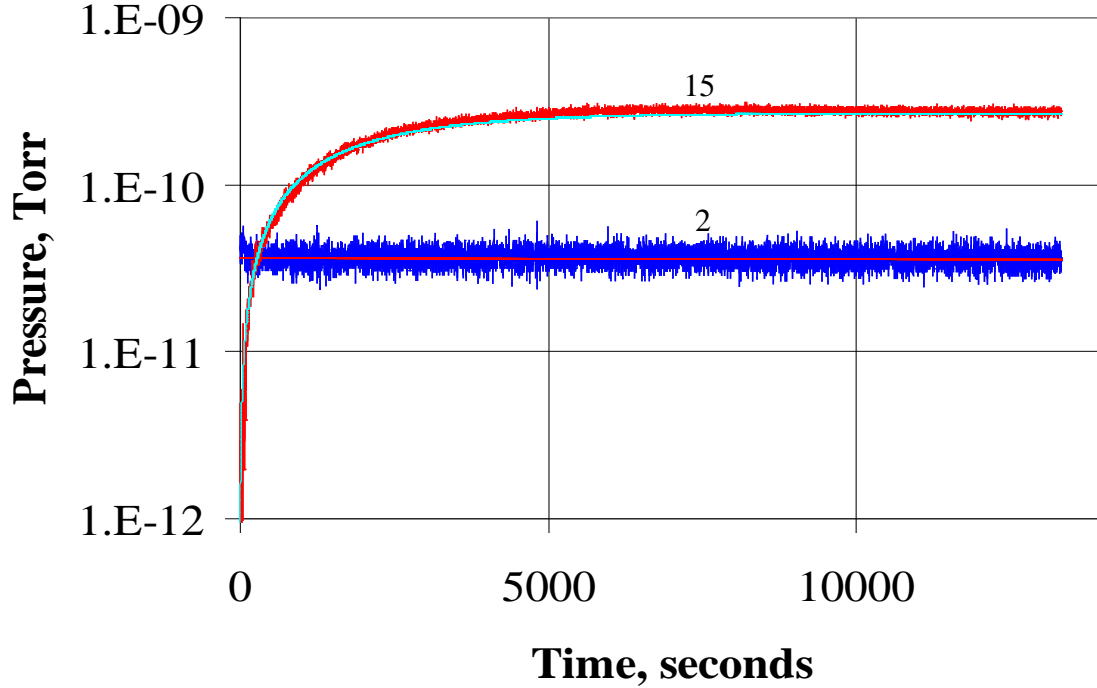

Figure 5. Build-up of methane (mass 15) in an IPR of the test chamber. QMA1 on, V1 closed, V_{NEG} open. The hydrogen pressure remains constant. The fit of equation (5) is shown by the pale blue curve passing through the red curve of the measured mass 15. The hydrogen and the methane curves are denoted by their masses, 2 and 15, respectively. Hydrogen pressure constant at $3.75\text{x}10^{-11}$ Torr.

A similar IPR in a much smaller volume with no hydrogen pumping resulted in a small rise in pressure over time, but at a much higher hydrogen pressure, $\sim 10^{-9}$ Torr. Fitting (7) to the data shown in Figure 4 gives rates of: $\alpha = 1.34\text{x}10^{-4}$ s^{-1}, $\beta = 1.1\text{x}10^{-3}$ s^{-1}. The rate for the increasing hydrogen pressure is, $\gamma = 3\text{x}10^{-5}$ s^{-1} ($H = 1.15\text{x}10^{-9}$ Torr, uncorrected QMA reading). The fit to the data is extremely good in this case, see Figure 6, with the equation well within the noise of the measurement data. It would appear that the production and break-up rates for methane are a function of the hydrogen pressure. The methane mass production rates,

$$\dot{Q} = V\alpha H \tag{8}$$

are $\sim 2.3\text{x}10^{-12}$ mbar l s^{-1} and $\sim 1.9\text{x}10^{-12}$ mbar l s^{-1} at hydrogen pressures of $7\text{x}10^{-11}$ mbar and $1.7\text{x}10^{-9}$ mbar, respectively (all values are nitrogen equivalent pressures). These mass production rates are very similar although the hydrogen pressures differ by a factor of 24.
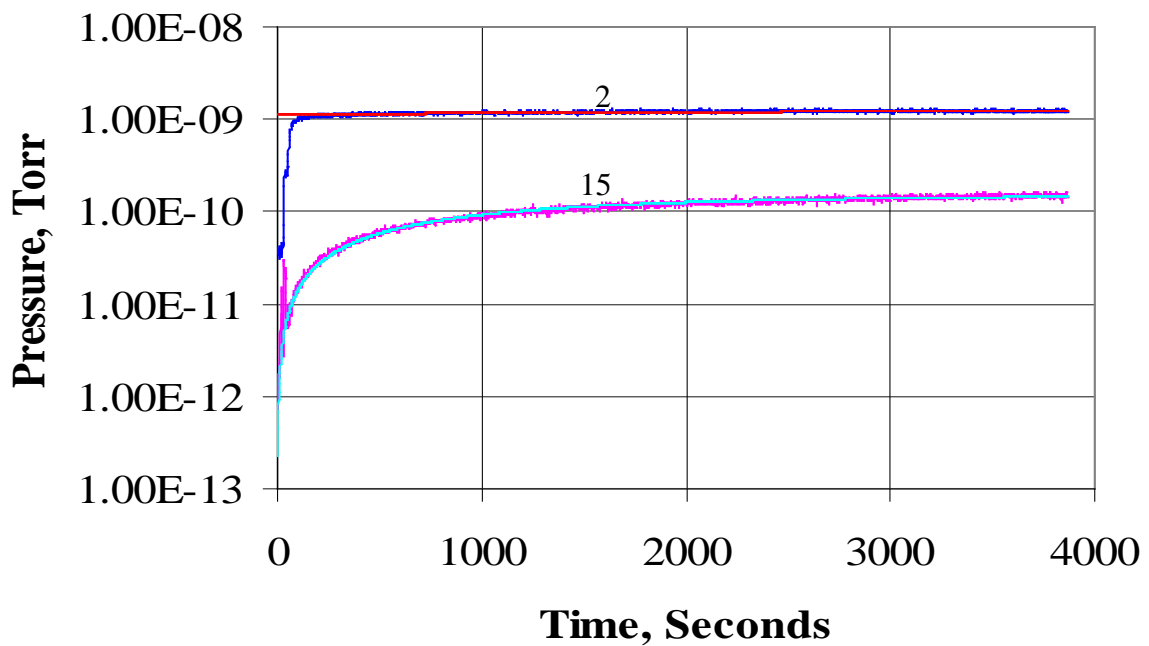
Figure 6. Build-up of methane pressure in an IPR of the volume between V1 and V2. QMA1 on, V1 and V2 closed. The fit of equation (7) is also shown by the pale blue line. The hydrogen and the methane curves are denoted by their masses, 2 and 15, respectively. The red line is equation (5).

5.2. Carbon Monoxide and Carbon Dioxide

It is not possible to measure unambiguously the real outgassing of these gases in the same way as for methane. The partial pressures of the gases were measured in the test chamber, with V2 closed and the NEG pumping, using a combination of the quadrupole analysers QMA1, QMA2 and QMA3. The partial pressures on one gauge were measured with no other gauge on, with one other gauge on and with two on. This was done for all combinations of the three gauges. The result showed that the hydrogen peaks were unaffected by the other gauges being on or off, but that the partial pressures of CO and CO_2 were proportional to the number of gauges that were on. It was concluded that within the accuracy of the measurements, the gauges produced >80% of these gases.

The measurements of the pressures of CO and CO_2 as the hydrogen pressure varied (see section 3) indicates that the pressures are a function of the hydrogen pressure. If the hydrogen pressure were zero then so would these partial pressures. Fremery [15] has shown these pressures to be proportional to the gauge emission current. Hence it is concluded that >80% of the gas is produced in the QMAs and in all probability this figure is 100%.

5.3. Water

Water is not increased when more gauges are operated, indicating that water is not produced in the gauges.

It will be seen from Figure 2 that the largest gas species is at mass 18 – water - on opening the valve V1 at the end of the long IPR. This is a surprising result and is unlikely to be produced by QMA3, since the mass 18 peak does not alter on closing V2 and the hydrogen barely increases on opening V1 (as the test chamber is pumped by the NEG). It is extremely surprising that the water should have risen to this level since it is pumped by the NEG.

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However, the NEG pumps the water at a slower rate, ~6 l/s, and has a smaller capacity (about 50 times less) than for hydrogen. It may be that the pump had become saturated with water during the IPR. The measured outgassing rate before the IPR was ~ 3×10^{-17} mbar l s^{-1} cm^{-2} for water, so the total quantity evolved during the 14 month IPR should have been 1.4×10^{-4} mbar l. The pump should have had a capacity of a few bar l for water. Thus the pump should not be anywhere near saturation. The result needs to be confirmed by further experiments.

5.3. Hydrogen

When the system was clean and had pumped for many days on the NEG pump, the measured hydrogen peak (mass 2) was 4×10^{-11} Torr on QMA1, QMA2 and QMA3. This corresponds to a partial pressure of hydrogen of 7×10^{-11} mbar, when corrected for the gauge sensitivity, cracking pattern and the helium calibration. The NEG has a speed of ~30 l/s for hydrogen from a previous calibration, so the specific outgassing rate of the stainless steel sheets is $g = 1.7\times10^{-14}$ mbar l s^{-1} cm^{-2}. This compares favourably with the previous measurement [12] of these sheets of ~3×10^{-13} mbar l s^{-1} cm^{-2}. It would appear that the benefits of the low temperature air bake are still present after 10 years, and indicate that the process gives stable long-term results. Presumably the reduced outgassing rate is due to the further vacuum bake, even though at the modest 150ºC.

If the QMA pumps the hydrogen and is able to maintain a pressure of ~1.8×10^{-9} mbar with no other pumping, the speed of the gauge is 1.2 l s^{-1} for hydrogen.

6. Outgassing

Fremerey [15] has recently commented that it is now being accepted that the outgassing constituent of stainless steel is virtually all hydrogen. He justifies his statement from the reports from other investigators [13,16], with the results obtained in plasma physics [17] and from his own measurements admitting hydrogen to the system and showing the production is proportional to the ion current. However, he does not show conclusively that these gases are not outgassed at some level, whereas this work attempts to quantify the maximum outgassing rate of methane, carbon monoxide, carbon dioxide and water.

Fremerey [18] proposes a new definition of pressure measurement at low pressures where the gauges interfere with the readings. Using the rate of rise of the pressure, dp/dt, in an IPR of a system with a pump down time constant of τ_p, the base pressure is defined by,

$$p = \frac{1}{\tau_p}\frac{dp}{dt}$$

(9)

The rate of rise is measured by a spinning rotor gauge, which should not produce gases as in gauges employing ionisation.

The gas in a vacuum system in equilibrium is the resultant of the loss and capture of gas from the walls and the pump (assuming no gauges creating gas). In a sealed system (no pump) the gas in the system is the result of the loss and capture rates from the walls alone. Elsey [19] and Hobson [20] have pointed out the difference between the "true" and the "net" outgassing rates, the latter being generally measured. The system pressure will reach equilibrium when these competing processes are equal.

In general it is possible to consider a surface with sites that will allow the residual gas molecules or atoms to reside for varying lengths of time [1]. As a surface is pumped and outgassed under heating or bombardment by particles or electromagnetic radiation, the surface will start to become depleted with gas remaining on the sites of highest binding energy. Stainless steel is a complicated material consisting of a number of different metals with oxide layers on the surface; in addition, due to the manufacturing process, there is carbon and hydrogen present in the material as well as many other "impurities". There is evidence that hydrogen diffuses slowly from the steel at room temperatures [21 Calder and Lewin]. In

addition, desorption from the surface must be considered independently of diffusion [22 Moore]. The oxide layer can reduce the rate of loss, though whether by a barrier effect or by stronger bonding to the surface (or by the provision of more suitable sites) is unclear.

At the end of the long IPR measurement reported in this paper, the largest peak was mass 18 – water. There is some evidence that the hydrogen is converted to water, presumably by interaction with the oxygen on the stainless steel surface. This latter is an interesting if not worrying effect since it implies that the system may never be in simple equilibrium with just hydrogen coming off the surface. The method of Fremery [18] for measurement using the spinning rotor gauge in an IPR will not be so useful in this case since it can not measure the partial pressures of the different gas species.

6. Conclusions

It is very likely that methane is not outgassed from clean stainless steel; the methane is all due to production in the QMA. In addition, the outgassing of CO and CO_2 is at least an order of magnitude smaller than the values measured in this experiment. In all probability these gases are also totally produced in the gauges. The water is still problematical and requires further study, but indications are that it is produced by interaction of the hydrogen with the oxygen on the surface of the stainless steel.

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