THERMAL OUTGASSING

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Abstract
The physics and practical consequences of thermal outgassing in vacuum chambers are described in this article.

1. INTRODUCTION

Outgassing means usually two things (Fig. 1):

1. Molecules diffusing through the bulk material of a vacuum chamber, entering the surface and desorbing from it.
2. Molecules which have been adsorbed previously, usually during venting of the vacuum chamber, that desorb again, when the chamber is pumped to vacuum.

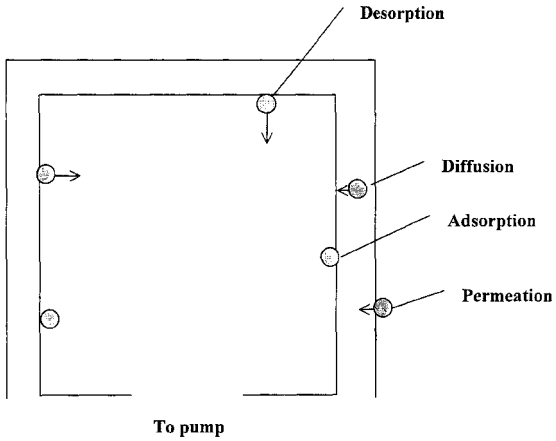


Fig. 1 The main physical effects which occur for thermal outgassing in a vacuum chamber.

Both effects have the same consequences: they limit the lowest achievable pressure in a vacuum chamber, they considerably extend the time for high and ultrahigh vacuum to be reached, and the outgassing molecules are a source of impurities in a vacuum chamber which is, for example, extremely inconvenient in the semiconductor industry. Especially in metallization processes, oxygen contaminants are disastrous because they reduce conductivity, and the smaller the structures on the integrated circuit (IC), the fewer particles can make it fail. In accelerators the residual gas particles limit the performance and its life time and can finally make high energy physics experiments impossible. In gravitational wave observatories the residual gas may limit the resolution of Michelson interferometers.

A further source of outgassing is the vaporisation or sublimation of atoms or molecules from a material with a vapour pressure higher or comparable to the vacuum pressure to be applied to a chamber. Although this fact is trivial, it greatly limits the number of materials that can be used in high and ultrahigh vacuum chambers and can sometimes be a difficult problem to overcome. But the careful selection of materials will not be the subject of this paper and we restrict ourselves to the effects of desorption, out-diffusion and permeation of materials suitable for UHV applications.

2. PUMP-DOWN BEHAVIOUR AND DESORPTION

Consider a perfect vacuum vessel, meaning a vessel with zero leakage, gas permeability and outgassing. Suppose that it is of volume V and pumped by a pump with zero ultimate pressure and a volumetric pumping speed S. If at time t the pressure is p, the pressure-time relation is

$$V\frac{dp}{dt} = -Sp(t) \tag{1}$$

or

$$p = p_0 \exp(-\frac{S}{V}t) \tag{2}$$

where p_0 is the pressure at the beginning of pumping. On a ln*p* versus time plot the pressure decrease will be linear. *V/S* can be considered as the time constant of the system.

In a real chamber, in the initial phase of pumping there will be this linear behaviour in a ln*p* versus time plot [1], but then there will be a much slower decrease with much longer time constants than *V/S* with finally an asymptotic behaviour. If the chamber had been exposed to atmospheric pressure before, this is due to gas adsorbed on the surface that desorbs only slowly under vacuum. The rate of desorption will depend on the binding energies of the various gases to the surface, the surface temperature and surface coverage. Desorption outnumbers the effect of out-diffusion greatly in this initial phase.

Adsorption takes place by physical adsorption or chemical adsorption. In physical adsorption gas molecules are attracted weakly by van der Waals forces with binding energies of less than 40 kJ/mol (10 kcal/mol or 0.4 eV), in chemisorption actual chemical bonding occurs between the gas molecules and the molecules and atoms on the surface of the vacuum material. These binding energies vary between 80 kJ/mol and 800 kJ/mol (20 to 200 kcal/mol or 0.8 to 8eV).

The quantity of gas adsorbed at constant temperature on a given surface increases with the pressure of gas in the gas phase. The relationship between the quantity adsorbed and the pressure is called the adsorption isotherm. There exist several models to describe these isotherms, the three most important can be attributed to Langmuir, Freundlich, and Temkin (Fig. 2).

Langmuir-Isotherm

The Langmuir Isotherm assumes that the adsorption energy is independent of surface coverage. It is therefore applicable, where surface coverage θ is low ($\theta < 0.3$).

Freundlich-Isotherm

This assumes that the adsorption energy decreases exponentially with surface coverage. It is applicable to higher surface coverages.

Temkin-Isotherm

This assumes that the adsorption energy decreases linearly with surface coverage.

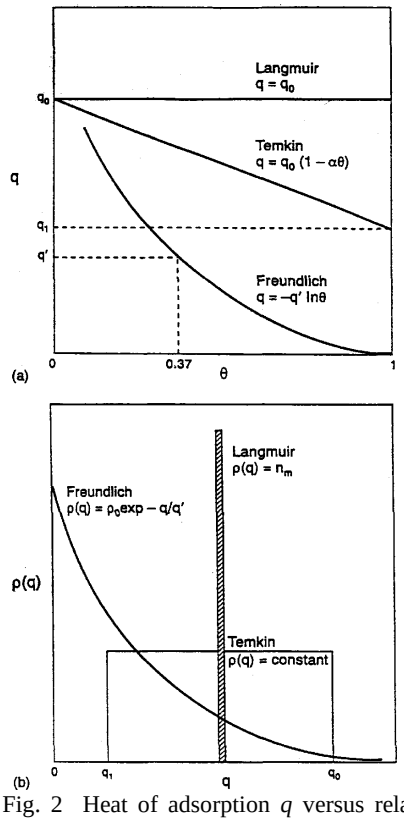


Fig. 2 Heat of adsorption *q* versus relative surface coverage (θ = 1 monolayer coverage) for three major isotherms (top) and the corresponding density of adsorption sites ρ as a function of *q* (bottom). From Ref [5]. Copyright American Vacuum Society.

The desorption rate can be described by

$$\frac{dn_S}{dt} = -\nu_0 n_{mon} f(\theta) \exp\left(E_{de} / RT\right) \tag{3}$$

With n_S the number of molecules on the surface, n_{mon} number of molecules in a monolayer, ν_0 frequency of oscillation of a molecule on the surface, *f(θ)* function of surface coverage (isotherm function), and E_{des} the activation energy for desorption.

The residence time τ of a particle on the surface can be described as

$$\tau = \frac{1}{\nu_0} \exp\left(E_{des} / RT\right) \tag{4}$$

For $\nu_0 = 10^{-13}$ s^{-1}, E = 42 kJ/mol and T = 300 K this gives τ = 2 µs. Gases that are physisorbed desorb very quickly at room temperature.

It is possible to derive an equation for the pump down:

- Gas removed by the pump: $n_V\ c/4\ A_p$ (n_V molecule density in the volume, c mean thermal velocity, A_p effective pump area.
- Gas desorbed from the surface: $n_S/\tau\ A_S$ (n_S number density of molecules on surface A_S surface area).
- Gas being re-adsorbed on the surface: $n_V\ c/4\ sA_S$ (s sticking probability).

So, finally

$$V\frac{dn_V}{dt} = -\frac{c}{4}n_V A_p + \frac{n_S A_S}{\tau} - \frac{c}{4}n_V sA_S \tag{5}$$

where at the same time the equation

$$A_S\frac{dn_S}{dt} = -\frac{n_S A_S}{\tau} + n_V\frac{c}{4}sA_S \tag{6}$$

has to be fulfilled for the surface. From Eq. (6) it can be seen that the net outgassing rate for desorbing gas particles depends generally on pressure.

Combining the two equations gives a differential equation for n_V

$$\frac{d^2 n_V}{dt^2} + \left(\frac{c}{4V}\left(sA_S + A_p\right) + \frac{1}{\tau}\right)\frac{dn_V}{dt} + \frac{c}{4V}\frac{A_p}{\tau}n_V = 0 \tag{7}$$

With some simplifications, Hobson [2] has plotted a solution of this equation for various values of E_{des} that you can often see in the literature. The system shown in Fig. 3 has been calculated for V = 1 L, A_S = 100 cm^2 and S = 1 L/s, first-order desorption and T = 295 K. Hobson also assumed a pressure independent sticking probability, which is a simplification that limits the usefulness of this approach. As in a pump down of a system without desorption (Eq. (2)) the logarithmic pressure falls with the inverse of time, but with time constants generally much greater than V/S.

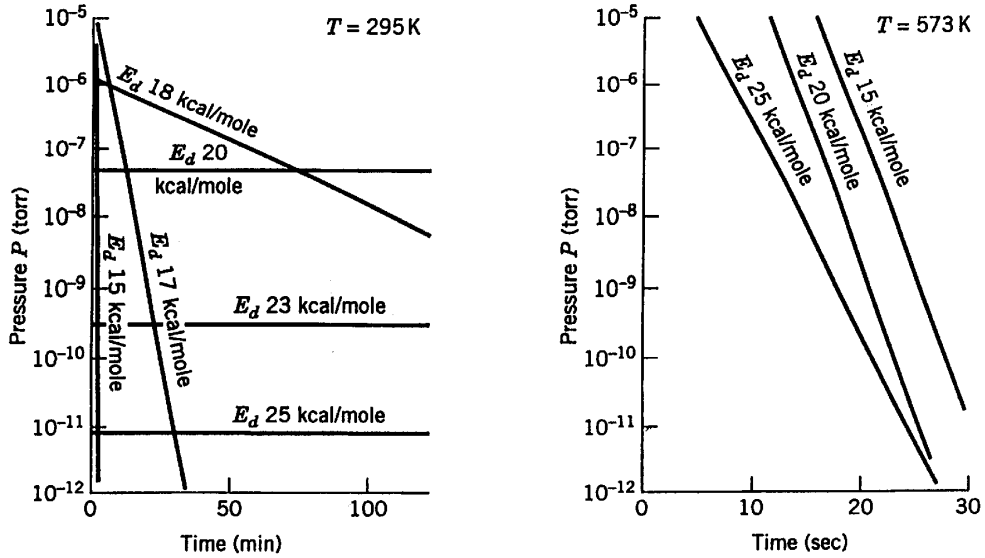


Fig. 3 Calculated pressure vs. time curves for the pumpdown of vacuum chambers having adsorbed layers with the adsorption energies indicated. From Ref. [3]. Copyright 1961 American Vacuum Society. Reprinted by permission of John Wiley & Sons, Inc

Two points can be concluded from Fig. 3. For small values of E_{des} the desorption rates are so high that the corresponding molecules quickly disappear out of the volume and cause no further problem. For very high values of E_{des} the desorption rates are too small to be of any consequence. It is only the intermediate range that is really troublesome since gas cannot be eliminated from the vacuum system in a reasonable time.

And what nature did was to put the desorption energy of water on stainless steel and aluminium exactly in this intermediate range. The desorption energy of water on these surfaces lies in the range of 80 to 92 kJ/mol (19 to 23kcal/mol). So, at the start of pumping, H_2O will be the major component (about 85% [3]) in the system and this will continue to be for days and weeks, if nothing is changed. Other minor outgassing molecules are H_2, CO, CO_2 and CH_4 [2]. We note at this point that H_2O-outgassing is not only generated by molecules previously adsorbed, but also by the reaction of iron oxides [4] in the case of stainless steel:

$$Fe_xO_y + 2H \rightarrow Fe + H_2O$$

In real systems the net desorption rate will follow a power law

$$q_d = Kt^{-n} \tag{8}$$

and when the pumping speed is constant, the pressure in the system will follow

$$p = kt^{-n} \tag{9}$$

Several authors have measured *n* and it typically varies between 0.9 and 1.3. This indicates that there is more than one type of adsorption site for water as is also clear from the fact that a technical surface is not uniform but very complex and it is rather improbable that there would be only one desorption energy possible. Recently, Redhead [5] has explained the approximate t^{-1} behaviour by a distribution of binding energies (Fig. 4), whereby several isotherm gave the same general behaviour.

However, another model has been proposed to explain the t^{-1} behaviour of the pump-down curve. Dayton [6] suggested a mechanism based on the diffusion of water vapour molecules out of capillaries in a thin oxide layer covering the metal surface. We will see later that for the case of diffusion the outgassing rate or pressure varies with the square root of the pumping time, whereas a t^{-1} behaviour has to be explained. The Dayton theory assumes that diameter and length of pores and capillaries in the surface oxide layer vary, giving rise to a range of diffusion coefficients. A time constant τ is introduced and when the pumping time is greater than τ, the outgassing should start to decay exponentially. With a distribution of τ, the final sum curve will also follow a t^{-1} behaviour (Fig. 5).

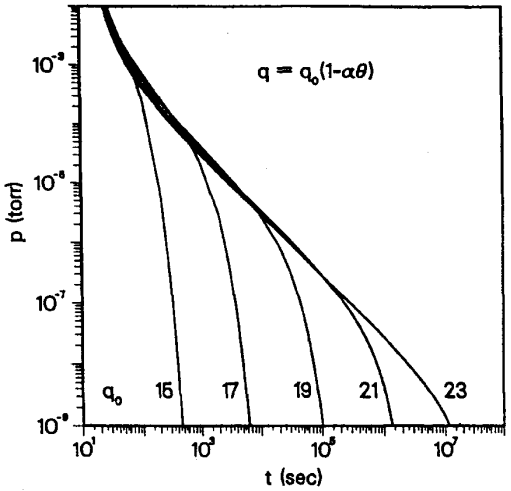


Fig. 4 Calculated pressure vs. time for a chamber with an adsorbed layer obeying the Temkin isotherm. From Ref. [5]. The sum of the curves follows approximately the experimentally observed t^{-1} behaviour. Copyright American Vacuum Society.

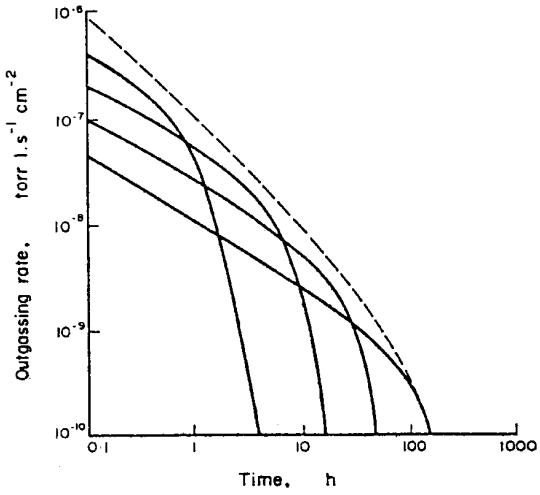


Fig. 5 Temperature dependence of CO outgassing of stainless steel showing different activation energies above and below about 250°C. From Ref. [7]. Copyright American Vacuum Society.

In conclusion, from the very easily measurable pumping curve useful information can be obtained, especially in practice where after a while one has specific experience how the system pumps down. By comparison of a pumping curve to a normal one, one can easily detect problems

such as a virtual or real leak, because in this case the logarithmic pump down curve versus time will approach asymptotically a constant pressure value, determined by the leak rate divided by the pumping speed, instead of falling with t^{-1}. But also theory can draw useful information from a pumping curve, because different isotherms give different pumping curves. Redhead [5] found that the Temkin isotherm without any approximations gave the best results compared with experimental data.

3. VACUUM SYSTEMS AFTER BAKE-OUT AND OUT-DIFFUSION

The clear conclusion from Fig. 3 is that a vacuum chamber has to be heated up to remove the adsorbed gas molecules with binding energies in the range of 17 to 25 kcal/mol or somewhat higher. To what temperature and for which time length a system has to be raised to remove adsorbed molecules, namely H_2O, is dependent on the ultimate pressure that is desired after bake-out and cool-down to room temperature, on the binding energies of the adsorbed molecules, the material of the vessel and the sealings and on the surface of the vessel and its pre-treatment.

The latter two points are very important in the author's opinion, because the surface chemistry greatly depends on the material, its pre-treatment and temperature since the surface before, during and after a bake-out will not be the same. As an example, we report on measurements of Ishikawa and Yoshimura [7], who have analysed the temperature dependence of H_2, H_2O, CO, CO_2, and CH_4 outgassing of 316 L stainless steel (Fig. 6). They found a clear change of activation energy at 250°C for CO that also occurred for H_2O, CO_2, and CH_4. At temperatures > 250°C apparently these molecules are chemisorbed whereas they are only physisorbed below 250°C.

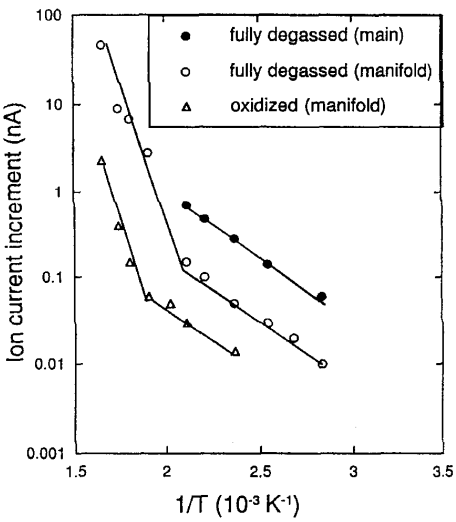


Fig. 6 Temperature dependence of CO outgassing of stainless steel showing different activation energies above and below about 250°C. From Ref. [7]. Copyright American Vacuum Society.

It is not as simple as was thought with early UHV metal systems that a system has to be baked to as high a temperature as possible, usually to more than 350°C, to remove all water from the system to obtain the lowest outgassing rates. Perhaps this view came from experience with the previously used glass systems, which contained a large amount of dissolved water which had to be removed at temperatures up to 500°C. We will come back to this point when we have further discussed the problems of out-diffusion, permeation and pre-treatment. Because today's vacuum systems are almost exclusively manufactured from stainless steel or aluminium, only these materials will be discussed in the following.

It should be noted here that for bake-out ion pumps should not be used since they soon saturate and give a poor ultimate pressure after bake-out, and re-emission of pumped gases may also occur.

Let us suppose that, after a successful bake-out of a metal vessel, all physisorbed and chemisorbed molecules have been desorbed and the surface is clean in this sense. Now, a different mechanism of outgassing comes into action. Hydrogen atoms dissolved in the bulk diffuse to regions where the hydrogen concentration is lower. The region under the vacuum surface is such a region, because eventually hydrogen atoms diffuse to the surface and recombine with a second hydrogen atom by surface diffusion which enables the molecule to desorb from the surface since the desorption activation energy of H_2 is rather low. In a quasi-static equilibrium there will be a constant net flow of hydrogen atoms to the vacuum surface which then desorb.

Two questions have to be answered at this point:

1. *Why is hydrogen present in the metal and can one avoid it being dissolved there?*

Hydrogen has a very small atom with the lowest possible mass, has a high solubility in most metals and diffuses easily through them. During the production of stainless steel, when it is molten, hydrogen, which is contained in air with about $4 \cdot 10^{-2}$ Pa diffuses quickly into the metal. An obvious cure would be to carry out this process under vacuum. This is actually done for some alloys, but one has to remember that this vacua, in a rough industrial environment at very high temperatures is only of the order of 10 Pa. Additionally, the material after cooldown is processed with acids to remove thick oxide layers in order to be able to roll the steel and, probably, allows hydrogen to diffuse into the material.

2. *What is the rate of diffusion to the surface?*

The theory to solve this problem is discussed in another article of this volume. The result for an infinitely large sheet of metal (a sufficient approximation, because the thickness of all metal sheets is much smaller than the lateral dimensions). With thickness 2*d* (defined in this manner for symmetry reasons) and initial concentration c_0 the flow of atoms to the surface is

$$j_{diff} = \frac{2D}{d} c_0 \sum_{i=0}^{\infty} \exp\left(- \frac{(2i-1)^2 \pi^2}{4d^2} Dt \right) \tag{10}$$

with the temperature dependent diffusion coefficient

$$D = D_0 \exp\left(- E_{diff} / kT\right) . \tag{11}$$

The characteristic time constant

$$t_c = \frac{4d^2}{\pi^2 D} \tag{12}$$

is strongly temperature dependent. For times $t > 0.5\ t_c$ the higher orders of $i > 0$ contribute with less than 2% to the total sum [8] and Eq. (10) can be simplified

$$j_{diff} \approx \frac{2D}{d} c_0 \exp\left(- t / t_c\right) . \tag{13}$$

For much smaller times

$$j_{diff} = \frac{2D}{d} c_0 \sqrt{\frac{\pi t_c}{16t}} . \tag{14}$$

We firstly estimate t_c for stainless steel with $D_0 = 0.012$ cm^2/s, $E_{diff} = 0.56$ eV, $T = 300$ K, $d = 1$ mm to $t_c(300\ \text{K}) = 1.8 \cdot 10^9$ s (57 years), while $t_c(1200\ \text{K}) = 92$ s.

Therefore, for the room temperature case and the stainless steel never heated since production ($c_0 = 0.4$ mbar l/cm^3)

$$j_{diff}\,(10^7\,s) \approx 10^{-10}\,\text{mbarl/scm}^2$$

We have chosen 10^7 s (116 days) as an average time between manufacturing the stainless steel and first pumping a vessel made from it. Although this outgassing rate is sufficient to reach HV, it is not for UHV (consider $A_S = 10000$ cm^2, $S = 100$ L/s, it follows that $p = 10^{-8}$ mbar or 10^{-6} Pa). It would take a factor of 100 longer time, that means 30 years, to decrease this outgassing value by a factor of 10!

However, because we want to desorb adsorbed molecules from the surface, let us suppose, we made a 24-h in-situ bake-out at 250°C of our vacuum chamber (in-situ bake-outs are carried when the vacuum system is completely installed and in operation). Due to the much higher temperature the concentration profile of the hydrogen will be determined during the bake-out time which is then ‘frozen-in’ at room temperature. Again, for $t > 0.5\ t_c$ one obtains

$$j_{diff} = \frac{2D_r}{d} c_0 \exp\left(-\frac{\pi^2 D_1 t_1}{4d^2} \right) \tag{15}$$

where D_r is the diffusion coefficient at room temperature, D_1 at bake-out temperature and t_1 the bake out time. t_c(523 K) = 25 h, so that Eq. (15) can be applied. We obtain under the described bakeout conditions

$$j_{diff} \approx 6 \cdot 10^{-12} \text{ mbarl/scm}^2 \tag{16}$$

which is constant for practical times. This value is already acceptable for modest UHV applications, and an ultimate pressure of $6 \cdot 10^{-10}$ mbar ($6 \cdot 10^{-8}$ Pa) can be expected (A_S = 10000 cm^2, S= 100 L/s as above). A second bake-out would reduce the outgassing rate by a factor of 2.6 according to this calculation.

4. PRE-BAKE-OUTS TO REDUCE OUTGASSING

To further reduce outgassing rates below a level of 10^{-12} mbar l/s cm^2, Calder and Lewin [9] investigated in the 1960s, how high-temperature pre-bake-out in a vacuum furnace could be used to degas hydrogen from stainless steel to reduce its bulk concentration (pre-bake-outs are carried out before the vacuum system is installed). Since Dt appears in the exponent and D is exponentially dependent on temperature it seems much more effective to increase the temperature of the bake than to increase the bake-out time.

With their available data, Calder and Lewin calculated that a 1-h bake at 1000°C would decrease the outgassing rate at room temperature to the same level as a 300°C bake for 2500 h. From the permeation of hydrogen from the atmosphere into the material during in-situ bake-outs and the resulting outgassing rate at room temperature, they concluded that outgassing rates as low as 10^{-16} mbar l/s cm^2 could be achieved. Their experimental values were two orders of magnitudes larger, but were attributed to limitations in their apparatus. However, many other investigators after Calder and Lewin failed to reach lower outgassing rates than 10^{-14} mbar l/s cm^2.

From our present knowledge, Calder and Lewin were in error for several reasons:

1. Their diffusion coefficient values were based on an investigation by Eschbach [10] in 1963. These values were determined by measurements of the permeation of hydrogen through stainless steel. In later investigations it became clear that the surface oxide plays a very significant role when permeation rates are measured. Louthan and Derrick [11] have carried out a very careful experiment to measure the permeation rate of deuterium through austenitic stainless steel. The diffusion coefficient of hydrogen and deuterium is very much the same and should scale with the square root of the mass, which is probably within the uncertainty of the experimental values. Hence the hydrogen diffusion coefficient should be larger by 1.4. Louthan analysed the time-temperature dependence of deuterium flux through austenitic stainless steel foils which were in contact with lithium deuteride (LD) powder to prevent oxidation of the steel surface by $Cr_2O_3 + 6LiD \rightarrow 3Li_2O + 2Cr + 3D_2$. There are also similar reactions to reduce iron and nickel oxides. Louthan found large differences of permeation rates depending on surface preparation which, at a given temperature, were orders of magnitude different. Their final result for the diffusion in 304 type steel (304, 304N, 304L) was:

$$D = 6.6 \cdot 10^{-3} \exp\left(-\frac{12.9 \text{ kcal/mol}}{RT} \right) \text{cm}^2/\text{s} \tag{17}$$

where 12.9 kcal/mol correspond to 0.56 eV. At room temperature this gives a value of $2.4 \cdot 10^{-12}$ cm^2/s to be compared with Eschbach's value of $5 \cdot 10^{-14}$. This is consistent with the observation of Louthan that oxide layers as probably present in Eschbach's experiment reduce the permeation rate significantly.

The consequence of higher diffusion of hydrogen in stainless steel is that Calder and Lewin underestimated the total outgassing rates at room temperature according to their pure diffusion

limited theory, but their general conclusions are true in both cases (for example that a 1-h bake out at 1000°C is completely sufficient).

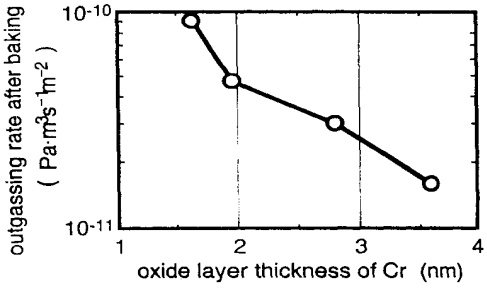


Fig. 7 Outgassing rate after in-situ baking as a function of the oxide layer thickness on stainless steel. Reprinted from Vacuum, 47, K. Odaka and S. Ueda, p689, Copyright (1996), with permission from Elsevier Science

2. Their second error is related to the fact that surface layer effects were neglected. For the example of the permeation rate measurements, we have already seen that oxide layers play a significant role. If we believe that Eschbach's measurements were correct, but taken from a technical surface with a normal oxide, and consider the results of Louthans from an oxygen-free stainless steel surface, than the effect of the surface layer is about a factor of 40 at room temperature. Other investigators have collected data that surface layers significantly affect outgassing rates. Odaka and Ueda (Fig. 7) have determined outgassing rates depending on the Cr-oxide layer thickness on stainless steel [12]. The outgassing rate at 3.6 nm thickness was about a factor of 5 lower than with 1.6 nm thickness.

3. An error, closely related to this, is that the permeation measurements were carried out with pure hydrogen. Eschbach, however, noted that adding a few Torr of oxygen to the hydrogen caused the permeation to decrease by a factor of 10 or more. Considering that in air 159 Torr (21 kPa) are present the reduction effect is probably much greater than a factor of 10, perhaps 100.

4. When a hydrogen atom has moved to the vacuum surface, it needs another hydrogen atom on the surface to recombine. The smaller the number of freely-movable hydrogen surface atoms, the less probable is recombination. This means that when the out-diffusion of hydrogen atoms to the surface becomes small, the recombination of the hydrogen atoms might be the limiting step. The outgassing from the surface is then no longer given by the out-diffusion rate, but by the rate at which the hydrogen atoms can recombine. The assumption of Calder and Lewin in solving the diffusion equations, that the surface density of hydrogen is always zero, is therefore very questionable. In contrast, if the surface density was zero, the recombination probability would also go to zero and the number of hydrogen atoms would accumulate on the surface, until the rate of recombination equalled the rate of diffusion to the surface. Therefore, the surface density can never be zero and the diffusion equations have to be solved by a boundary condition, which takes the recombination into account. Moore [13] calculated this numerically and Fig. 8 shows the H concentration profile in the cross section of an infinite plate 1.9 mm thick during a vacuum furnace bake-out at 950°C. The label numbers are the bake-out time in seconds. Due to the finite concentration on the surface there is a major departure from the diffusion limited profile. As time increases, the distribution approaches a sine function plus a constant, instead of the pure sine function with pure diffusion limited outgassing. This sine component decreases as time goes by and after 2000s the concentration is practically uniform. This is the time where the outgassing is limited

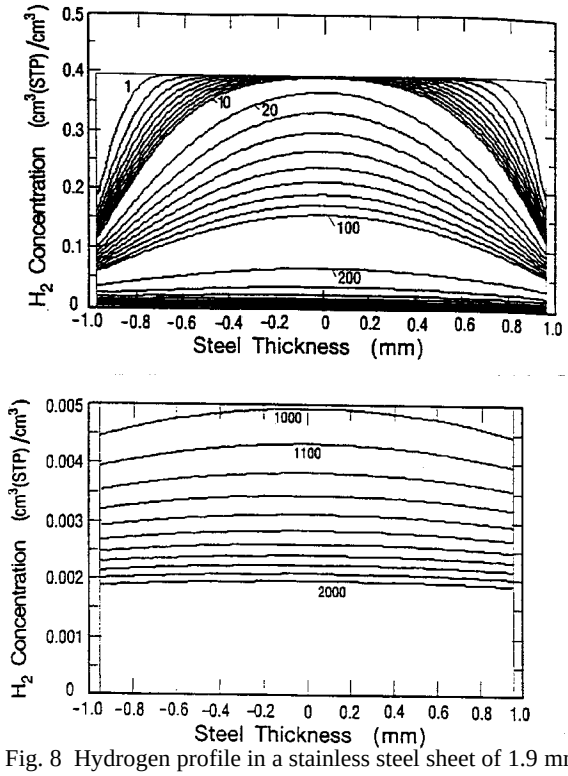


Fig. 8 Hydrogen profile in a stainless steel sheet of 1.9 mm thickness at 950°C with time as parameter in seconds. Calculations of Moore for recombination limited outgassing. The lower figure is an enlargement of the upper one for larger times. From Ref. [13]. Copyright American Vacuum Society.

by the recombination while the diffusion is still fast enough that every two surface atoms which recombine are immediately replaced.

When Moore analysed the outgassing rate versus time, he noted, that after about 1000 s the recombination limited outgassing will be orders of magnitudes higher than the results with the pure diffusive model. It is usually assumed that the recombination rate is proportional to the square of the number density of surface atoms n_S times a recombination coefficient K_{rec}

$$j_{rec} = K_{rec} n_S^2 \tag{18}$$

By fitting this model to experimental values [14], Moore was able to determine K_{rec} to $3 \cdot 10^{-22}$ cm^2/s at 950°C.

If the desorption of H_2 is governed by the recombination rate, the surface roughness, which affects surface diffusion, should also change the effective H_2 desorption energy. This was indeed indicated by experimental results from Chun et al. [15]

From Calder and Lewins work and their errors that have been described above, the following conclusions can be drawn:

1. Pre-bakes at high temperature are a very efficient way to reduce outgassing of hydrogen from stainless steel. For aluminium as vacuum material for XHV it is probably a great disadvantage that high temperature bakes (at least not with currently available alloys) are not possible.
2. The diffusion model which describes the outgassing only by the diffusion rate without considering the recombination process at the surface and the role of the oxide layer is not sufficiently accurate to predict temperatures and times needed for very low outgassing rates. Much longer bake-out times than calculated by Calder and Lewin are necessary to obtain outgassing rates < 10^{-14} mbar l/s cm^2.
3. Permeation rates as calculated by Calder and Lewin are probably too high by a factor of 100, maybe 10000.

That these conclusions are actually true, has recently been confirmed by Nemanic, Setina and Bogataj [16, 17]. They wanted to produce vacuum insulating panels without getters. For this reason, a material had to be found with outgassing rates so small that high vacuum could be kept for 10 years without pumping. This required a search for materials with outgassing rates below 10^{-15} mbar l/s cm^2. Their solution was to use a 0.15-mm austenitic stainless steel foil which was baked for 68 h at 265°C. They obtained outgassing rates of 10^{-17} mbar l/s cm^2. A thin material has the great advantage that much shorter times or lower temperatures can be applied, which can be seen from Eq. (15). If d is reduced by a factor of 10, $D_1 t_1$ can be reduced by a factor of 100 to get the same outgassing rate with the diffusion model. As we have learned, this model is insufficient, but predictions with the recombination model are rather difficult, because the extrapolated or measured recombination coefficients K_{rec} differ by 4 orders of magnitude [17]. Nemanic has used the dimensionless Fourier number F_0

$$F_0 = \frac{Dt}{d^2} \tag{19}$$

to characterise bake-outs. He found that F_0 of about 50 is required for outgassing rates as low as 10^{-15} mbar l/s cm^2 and with F_0 = 160 he was able to obtain $2 \cdot 10^{-17}$ mbar l/s cm^2. For comparison, F_0 = 13 for a 2-h bake at 1000°C of a 3-mm thick stainless steel plate. Fremerey [18] used a 25-h vacuum firing at 960°C instead of only 2 h, as was normal in the past, and obtained an outgassing rate of 10^{-15} mbar l/s cm^2.

In conclusion, if very low outgassing rates must be achieved, much longer bake-out times than in the past should be used for 2 mm to 3 mm thick stainless steel, or alternatively much thinner material should be used. Perhaps in future XHV chambers or CERN accelerator tubes will be built of

0.15 mm stainless steel foil, just enough to withstand atmospheric pressure, welded to stronger supports to support the structure.

We mentioned in the last section that the optimum value of bake-out temperature of an in-situ bake-out may strongly depend on the pre-treatment. Jousten [19] has measured outgassing rates depending on the bake-out temperature of a previously vacuum-fired stainless steel chamber and found the surprising result that lower bake-out temperatures gave lower outgassing rates (Fig. 9). The measurements were carried out with the pressure-rise method (see next section). The pressure rise was linear indicating that no significant amount of water desorbed from the surface but only hydrogen (see next section).

There are other effective procedures to reduce outgassing, for example oxidation of stainless steel in air at 200°C to 250°C [16, 17, 20, 21]. These generally give very low outgassing rates for hydrogen, but for thicker samples (> 2 mm) not as low as the described high-temperature bake-outs. An advantage of oxidation is that the number of carbon impurities present on the surface is greatly reduced [7] with the consequence that the production and outgassing of CO, CO_2, and CH_4 may be also reduced. Additionally, after a 250°C bake-out in air, iron oxide dominates Cr_2O_3 at the surface [7]. Iron oxide has an even lower diffusion coefficient than Cr oxide. However, if also the structure of iron oxide is of advantage (pores?, density?) is yet unclear and one has to be concerned about the loss of anti-corrosion effect. Another beneficial effect of the oxide layer is that the number of adsorption sites which have a high desorption energy are considerably reduced.

Another method to reduce outgassing is glow-discharge cleaning which has mainly been developed for cases where high-temperature baking was not possible, for example in fusion devices. This method seems to be beneficial when a chamber is made for plasma processing, because a plasma may liberate much more highly-bonded carbon oxides and hydrocarbons than can be removed by thermal methods. More information can be found in the 'Outgassing III' chapter by O. Gröbner in these proceedings. Generally, the outgassing rates at room temperature after glow-discharge cleaning are considerably higher than with the above mentioned thermal pre-bake-outs. Glow discharge cleaning can also be combined with oxidations.

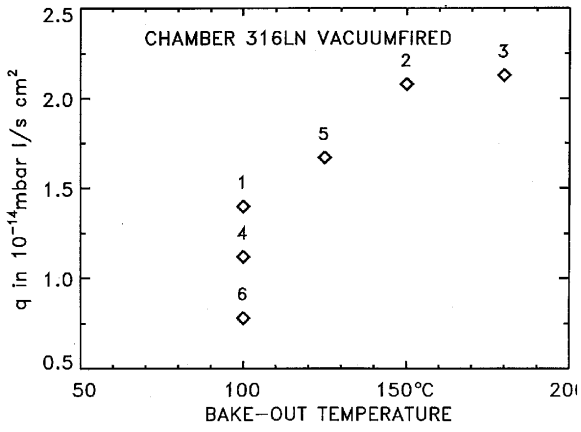


Fig. 9 Measured outgassing rate vs. bake-out temperature for a vacuum fired stainless steel chamber. The numbers follow the chronological order. Between each measurement the chamber was exposed to air and subsequently baked for 60h. From Ref. [19].

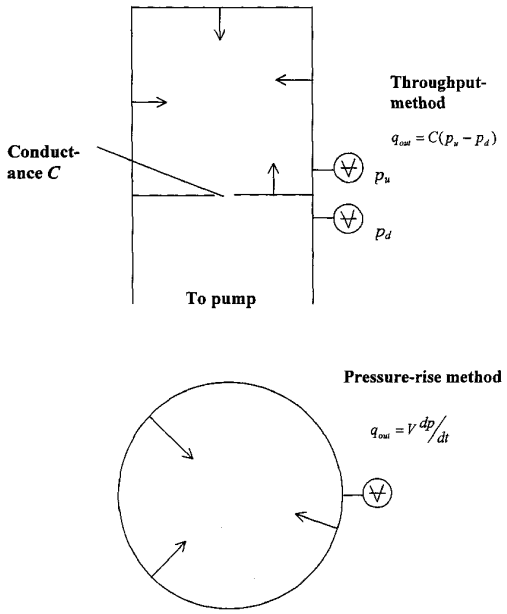


Fig. 10 Scheme showing the principal experimental set-up for the two main methods of outgassing rate measurement. In the throughput method the pressure drop across an orifice of known conductance is measured, in the pressure rise-method the accumulated gas pressure is measured in time.

5. OUTGASSING-RATE MEASUREMENT METHODS AND THE PROBLEM OF RE-ADSORPTION

Outgassing rates are measured by two general methods (Fig. 10): in the first, the chamber under test is pumped through an orifice of known conductance and the pressure drop across the orifice is measured as a function of time (outgassing rate may depend on time, as we have learned in sections 3 and 4). This is called the throughput method. In the second method, the pressure rise with time is measured in a closed system after evacuation to a low pressure. This is called the pressure-rise or gas-accumulation method. Both methods have a common problem: the measured outgassing rate is a net rate being the difference between the intrinsic outgassing rate of the surface and the readsorption rate. Papers containing published measurements rarely mention the difference between the two rates. It is widely assumed that outgassing rates measured by the throughput method can be applied to the design and analysis of vacuum systems with pumping parameters *S/A* (pumping speed divided by total area) and sticking probabilities that differ from the parameters of the system in which the outgassing rate was measured. So, be careful with the interpretation of results!

There is a third method using a direct molecular beam from a sample [22] and has the advantage that it directly measures net outgassing rates. Due to the need for cryogenic apparatus, it is however rarely applied.

Before discussing the problem of re-adsorption, however, let us first study the experimental methods in more detail. Figure 10 shows the basic scheme of an apparatus applying the throughput method. Two gauges can be used to determine the pressure drop across the conductance *C*, but very often it is assumed that the downstream pressure is negligible. This is a rather crude assumption when low specific outgassing rates ($<10^{-12}$ mbar l/s cm^2) are measured and should not be accepted in these cases. The gauges should be calibrated. The test sample can be either the chamber itself or a sample that is put into it. If a sample is used, a background measurement must be taken first without the sample. The total outgassing rate must be higher than the outgassing rate from the chamber to get a reasonably high signal. If this is not the case, the sample can be heated.

Since the pressures to be measured are usually very low in the throughput method ($<10^{-5}$ Pa), only ionisation gauges can be used for this purpose. This involves a big problem. Crossed-field ion gauges have the problem of a relatively high pumping speed that may be comparable to the conductance value of the orifice and would therefore significantly falsify measurements (indicating lower outgassing rates). On the other hand, you will hardly find a hot-cathode ionisation gauge with an outgassing rate $<10^{-11}$ mbar l/s. To get this low value, the gauge has to be specially prepared, degassed and evacuated over a long time. An outgassing rate of 10^{-11} mbar l/s can also be produced by 1000 cm^2 surface area with a specific outgassing rate of 10^{-14} mbar l/s cm^2. In this case an error of 100% would occur (indicating higher outgassing rates). Considering that normal hot ionisation gauges have outgassing rates of about 10^{-10} mbar l/s, it becomes clear that one of the first things that should be checked, when measuring total outgassing rates of this order, is the outgassing of the gauge.

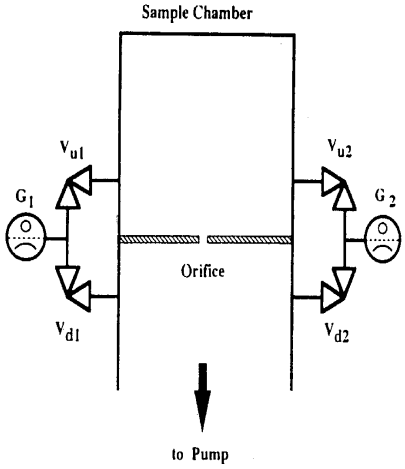


Fig. 11 Experimental set-up for the improved throughput method according to Yang et al. [23]. Two ionization gauges are used to eliminate effects due to outgassing of the gauges. Reprinted from Vacuum, 46, Y. Yang, K. Saitoh and S. Tsukahara, p1371, Copyright (1995), with permission from Elsevier Science.

Yang, Saitoh and Tsukahara [23] have proposed the following improvement to the throughput method (Fig. 11). They used two symmetrically arranged gauges, each separated by two valves from the upper and lower chamber. A single gauge can be used to measure both the upstream and downstream pressure. With the second gauge it is possible to measure the outgassing of the first gauge by taking the difference between the pressures measured with the valve V_{u1} open and closed.

Another variation of the throughput method is the so-called variable conductance or Oatley method [24]. The fixed conductance is replaced by a variable one or it is possible to replace the orifice in situ by a number of different conductances. The upstream pressure is measured depending on the conductance. If the outgassing rate is independent of the pumping speed, p versus $1/C$ will give a straight line. Deviations from it may indicate outgassing of the gauge or dependence of the outgassing rate on pumping speed or pressure (readsorption).

The pressure-rise method has similar problems to the throughput method if ionisation gauges are used. Outgassing of the gauge may indicate higher outgassing rates for the surface under investigation, while pumping by the ion gauge indicates lower outgassing rates. Therefore, usually, ionisation gauges are only switched on intermittently. But even in this case disturbances cannot be excluded. Another possibility is to accumulate the pressure in a chamber without any measuring device. Instead, a valve is opened after a certain time, and the pressure burst is measured by a total pressure gauge or QMS, that has to be calibrated for similar pressure bursts. The ideal choice of a gauge for applying this method is an inert gauge, which is now available in the form of the spinning rotor gauge. This gauge neither pumps nor outgasses. Although the residual pressure reading is only 10^{-6} Pa, in a pressure rise system this pressure is soon reached after only a few minutes, even when the outgassing rates are very low. When the pressure rise method is continued for days or even weeks, accurate measurements can be made. The pressure rise method has recently been successfully applied to determine very low hydrogen outgassing rates of UHV and XHV systems. The main problem in this method, however, is the effect of readsorption. If readsorption occurs, interpretation of results is even more difficult than in the case of throughput method, because the pressure and so the surface coverage is changing with time.

Redhead [25] has recently analysed the problem of readsorption on outgassing measurements, both for the throughput method and the accumulation method. For the throughput method he started with the conservation of mass, which requires that the flux of molecules leaving the surface is equal to the sum of the flux through the orifice, the flux of readsorbed molecules and the change in the number of molecules in the volume.

$$Aq_i = Aq_m + A\frac{p}{\sqrt{2\pi mkT}}s + KV\frac{dp}{dt} \tag{20}$$

where q_i is the intrinsic outgassing rate in molecules/s cm^2, q_m the measured outgassing rate (or the flux through the conductance), A total surface, s sticking probability, and K the number of molecules in a mbar l at 295 K.

The measured specific outgassing rate is given by

$$q_m = \frac{p}{\sqrt{2\pi mkT}}\frac{a}{A} \tag{21}$$

where a is the effective pump area.

In stationary state $dp/dt = 0$, so that

$$q_i = q_m + \frac{p}{\sqrt{2\pi mkT}}s \tag{22}$$

$$q_i = \frac{p}{\sqrt{2\pi mkT}}s\left(1+\frac{a}{As}\right) \tag{23}$$

$$\frac{q_m}{q_i} = \frac{\frac{a}{As}}{1+\frac{a}{As}} \tag{24}$$

This result is plotted in Fig. 12 (top) with the sticking probability as parameter. Typical experimental values of $a/A = 10^{-4}$, while sticking probabilities for water are between 10^{-1} and 10^{-3}. In this case,

ratios of q_m/q_i = 10^{-3} to 10^{-1} can be expected! For hydrogen the sticking probability is smaller, about 10^{-4}, so that the error in this case is less.

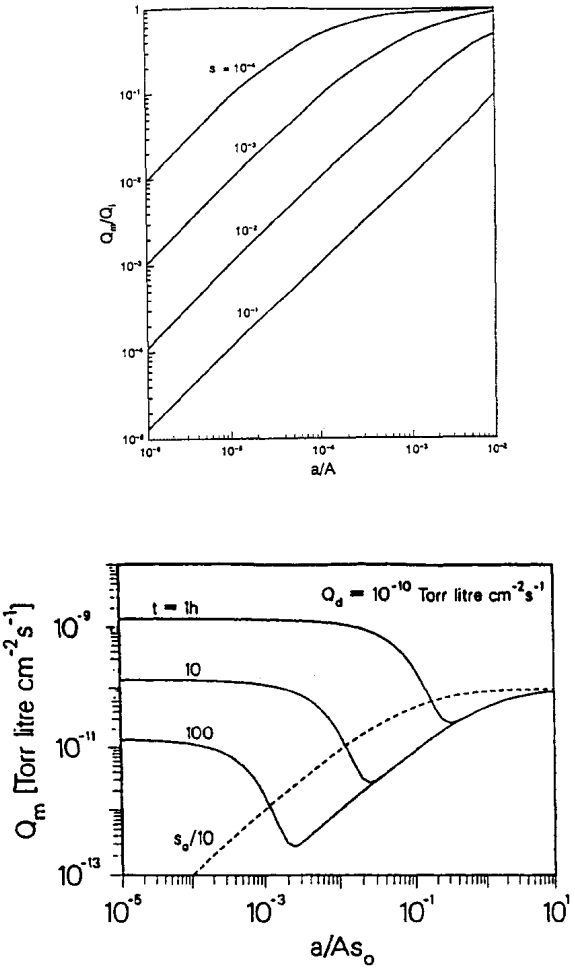


Fig. 12 Calculated ratio of the measured net outgassing rate to the intrinsic outgassing rate (Q_m/Q_i) in the throughput method as a function of the area ratio (open area to an ideal pump to total area) *a/A* with the sticking probability *s* as parameter (top) and the measured outgassing rate as function of *a/As* with pumping time as parameter (bottom). Outgassing by diffusion Q_d has been included in the lower figure. From Ref. [25]. Copyright American Vacuum Society.

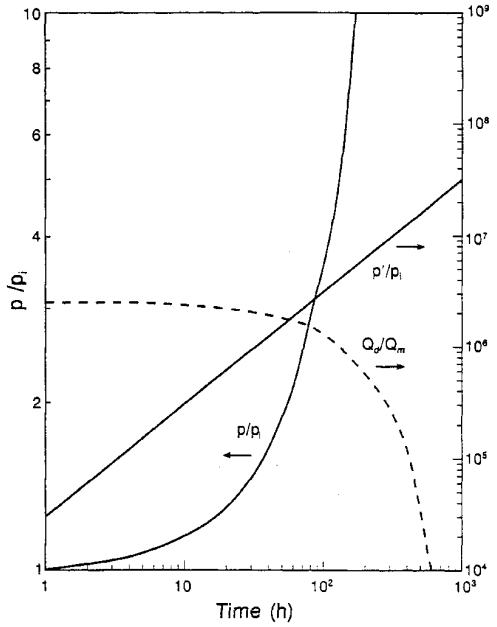


Fig. 13 Pressure rise-method: Calculated relative pressure rise (in units of initial pressure after closing the valve) versus time. From Ref. [25]. Copyright American Vacuum Society.

Another problem is how results from an outgassing measurement can be used under different pumping conditions. Figure 12 (bottom) shows the outgassing rates of H_2O, as they would be measured under different pumping conditions (*a/A*) and various pumping times. Also diffuse outgassing of 10^{-10} Torr l/s cm^2 was considered here. It is clear that the measured outgassing rate is a function of the pumping parameter and sticking probability for a/As_0 greater than some critical value. And the changes can be very significant (> factor 10). In the case of the accumulation method the pumping speed is zero and equilibrium adsorption isotherms can be used.

Figure 13 shows the increase of hydrogen pressure with time. *P'* is the pressure, if no readsorption occurs, *p* with adsorption, p_i is the pressure in the beginning of measurement when the pump valve is closed. It shows that the increase of *p* with readsorption is smaller by orders of magnitudes than without adsorption and far from being linear in time. Q_d/Q_m is the ratio of true outgassing rate to the measured outgassing rate.

Experimental curves of hydrogen outgassing, however, show a completely linear pressure rise over long periods of time (Fig. 14). What is the solution? It is well known that H_2 adsorbs significantly on stainless steel walls, when injected into a evacuated vessel, so an adsorption rate = 0 can be excluded, if the surface is empty. So, is the conclusion that all sites available for dissociative adsorption of hydrogen molecules are occupied? Redhead [25] could explain the experimental results with the following model:

1. The rate of hydrogen desorption is limited by the rate of recombination and by thermal desorption.
2. There is a number of type A sites accessible to H atoms from the interior. The diffusion rate is so high that, as soon as sites are emptied by desorption, they are immediately refilled from the interior.
3. There a number of type B sites that are not accessible to H atoms from the interior, for example due to an effective oxide layer, but these sites are involved in the ad/desorption cycles with H_2 in the gas phase.

After starting a pressure rise these type B sites will lead to readsorption, but will, because of their small number soon saturate and readsorption will cease. Redhead has calculated (for the experimental conditions of Fig. 14) what the ratio between the sites A and B may be to see a linear pressure rise. If $\sigma_B/\sigma_A \leq 30\%$, the pressure increases linearly after 1 h (Fig. 15).

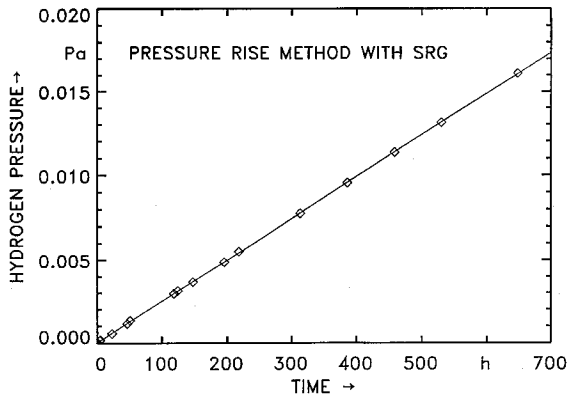


Fig. 14 Pressure rise method: Measured pressure rise in a vacuum fired stainless steel chamber with a spinning rotor gauge. Experiment carried out by the author.

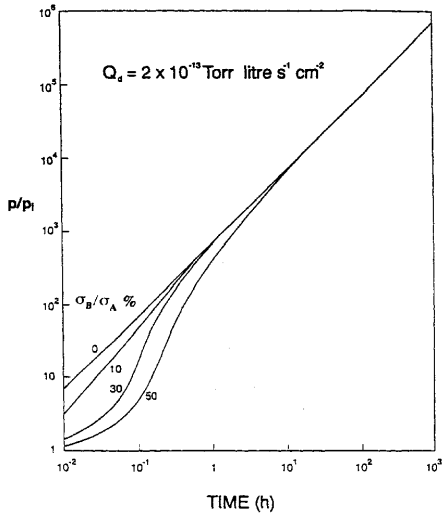


Fig. 15 Calculated relative pressure rise (in units of initial pressure after closing the valve) with the model introduced by Redhead. From Ref. [25]. Copyright American Vacuum Society.

From this model, which explains experimental results, we have another indication that at low outgassing rates the adsorption of hydrogen from a stainless-steel surface is not diffusion rate limited, but recombination limited. Otherwise it could not be explained why all available sites are always full. From the experimental data, and assuming desorption energies of H_2 between 18 and 24 kcal/mol, Redhead calculated the number of the available type A sites. This ranged from 10^{-4} to10^{-8} monolayers. This low value means that the distance between neighbouring sites is rather large and makes obvious the recombination as being the rate limiting process.

6. CONCLUSION

At the end of this review, it should be noted that the outgassing of materials both in theory and experiment is a very vivid subject, heavily discussed, and very complex, and there is still much to learn about it. The important problems will only be solved, if metal/material science, surface science and vacuum science work closely together.

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