AN UPPER BOUND TO THE PRESSURE IN AN ELEMENTARY VACUUM SYSTEM *

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ABSTRACT

MASTER

A vacuum system consisting of a volume V , a pump S and a
surface area A on which there are initially adsorbed $n(0)$ molecules
in a first order desorption state is considered and discussed. The
essential result is that $P_{\max} = 1.146 \times 10^{-5} \frac{A}{St}$ torr is expected to
provide a reasonably accurate estimate for the value the pressure
should be strictly less than t seconds after the pumping has started
given that the pressure in the system is due to an adsorbed surface
phase. Experimental tests of this relation have been performed and
comparisons are made between this result and the pressure measured
in an elementary vacuum system.

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I. Introduction

Consider a vacuum system consisting of a volume V (liter) contained by walls of geometric area $A(\text{cm}^2)$ and pumped by a S (liter/s) pump. The pressure p , t seconds after the pumping has started, is known¹ to result from gas evolution both from a surface phase adsorbed on the wall and from an absorbed phase which diffuses from the interior of the walls into the vacuum system. Since it is generally recognized¹ that a previously depleted absorbed phase is not replenished during a room temperature atmospheric exposure, it is assumed for the systems considered here that sufficient prior bulk degassing has taken place to reduce the contribution from this source to a negligible value. After this preparation the system, at temperature T_w , is given an exposure to atmosphere (or to some other volatile, non-corrosive gas). Without changing the system temperature, the exposure is ended, the pump started and $p(t)$ recorded. It is clear from previous studies^{2,3} that not enough basic information concerning molecular densities, binding energies, etc. is a priori available to determine $p(t)$. However an analysis is presented below which results in a determination of a value, P_{max} , the pressure should be less than t seconds after the pumping has started. It will further be seen that P_{max} is independent of T_w , wall material⁴ and exposure gas composition.

The remainder of this article has been organized in the following manner: in II the vacuum system is modeled and solutions

for $p(t)$ are found; in III $P_{\max}$ is derived; and in IV an experimental test of this relation is described and discussed.

II. System Model

The vacuum system considered is shown schematically in Fig. 1. The volume V is evacuated by a S (liter/s) pump and into this volume there is a real leak L . It is assumed that the walls contain a single first order adsorption-desorption state characterized by the rate constants (γ, E) and that the number of molecules/s entering this binding state is given by pS_w , where S_w is the wall pumping speed taken to be independent of the number adsorbed on the wall. Further, the number of molecules/s desorbing from the state (γ, E) on the wall is denoted by q_w where

$$q_w = \frac{n_w(t)}{\tau_w}, \quad \tau_w = (\gamma e^{-E/KT_w})^{-1}$$

where K is Boltzmann's constant, $n_w(t)$ is the number of molecules on the wall at time t , and (γ, E) are rate constants. τ_w is known as the sojourn time and in the absence of wall readsorption is the time required to decrease the molecular concentration in the state (γ, E) on the wall to $1/e$ of its initial value.

Since this system is similar to ones previously discussed,^{2,3} the solution will only be briefly developed. Conserving molecular flux both at the wall and in the volume of the system, the

following equations result:

$$\begin{aligned} L + q_w - pS_w - pS &= v \frac{dp}{dt} \\ pS_w - q_w &= \frac{dn_w}{dt} \end{aligned} \quad (1)$$

Combining these equations, a second order differential equation in n_w alone is obtained. The solution is found by elementary techniques and $p(t)$ is determined subject to the appropriate boundary conditions. The boundary conditions are specified by requiring a real leak L_0 be present from $t = -t_0$ (large) hence establishing equilibrium ($\frac{dp}{dt} = 0$) at $t = 0$ from which $n_w(0)$ and $p(0)$ are easily determined:

$$\begin{aligned} p(0) &= L_0/S \\ L_0 &= \frac{n_w(0)}{k \tau_w} \end{aligned} \quad (2)$$

where $k = S_w/S$. At $t = 0$ the leak is closed, simulating the end of the exposure, and the arbitrary constants determined by requiring n_w, p be continuous functions.

Although the exact solution is able to be obtained in the above manner, it is not instructive and it is in fact more useful to write an approximate solution as a series in δ :

$$p(t) = \frac{n_w(0)}{\tau_w S(1+k)} \left\{ \left[1 + \frac{2\delta}{(1+k)^2} + O(\delta^2) \right] e^f + \frac{1}{k} [1 + O(\delta)] e^g \right\} \quad (3)$$

where

$$\begin{aligned} f &= \frac{-t}{\tau_w(1+k)} \left\{ 1 - \frac{k\delta}{(1+k)^2} + O(\delta^2) \right\} \\ g &= \frac{-t(1+k)}{\tau_s} [1 + O(\delta)] \end{aligned}$$

where $\delta = \frac{\tau_s}{\tau_w}$, $\tau_s = V/S$, and $k = S_w/S$. For typical systems the soujourn times which will be of interest are greater than ~ 5 seconds whereas $\tau_s \leq 1$ second. Thus for these situations (3) should be reasonably accurate.

From (3) it is seen that there are two characteristic times during which the system pressure exhibits a change. The fast term ($\frac{e^g}{k}$) is significant for times $\sim \tau_s$ and only for small k . The slow term (e^f) has a characteristic time given by the product of τ_w with $(1 + k)$ and may be appreciably different from τ_w . This is particularly true for gases which have a high sticking probability upon impact on the wall of the vacuum chamber. For such a system k of the order of $10^3 - 10^4$ may be anticipated and illustrates the significant effect which wall readsorption may have on the pressure during pumpdown. For example, a gas whose soujourn time is measured in a separate experiment to be $\sim 10^3$ seconds on a surface may take $10^6 - 10^7$ seconds to leave a vacuum chamber whose walls are made of that material. This emphasizes the need to not only measure the binding energies of gases on vacuum chamber walls but also the pumping speed of the gas on the wall if accurate predictions of $p(t)$ are to be made on the basis of even a highly simplified model.

Figure 2 shows a numerical evaluation of $p(t)$ for a particular system with $\tau_w = 20$ seconds for various k . Seen in this figure is that for small k ($k = .001$) the system behaves as intuitively expected; i.e. in $\sim \tau_s$ seconds the volume gas leaves the volume and in $\sim \tau_w$ seconds the surface phase gas is removed from the system. It is further seen

that the time required for a change in pressure is correspondingly increased for large k even though τ_w has remained constant. This effect can be derived from physical arguments by noting that the probability v of a molecule leaving the system (entering the pump) each time it desorbs from the state (γ, E) is given by:

$$v = \frac{S}{S + S_w}$$

Now each time the molecule becomes adsorbed on the wall it is required to remain there, on the average, $\sim \tau_w$ seconds. In addition the average number of times n it becomes adsorbed in the state (γ, E) before eventually leaving the system is determined by $nv \approx 1$. Thus the average time τ it is in the system can be found and is given by:

$$\tau \approx n\tau_w = \tau_w(1 + k)$$

in agreement with our previous results, and emphasizes that the increased residence time of the molecule in the system is simply due to the surface readorption and re-emission.

In Fig. 3 a graphical solution for p is given provided that the other parameters are known⁶ (θ is defined as: $n_w(0) = 10^{15}\theta A_s$ molecules). One of the interesting features of this figure is that for any (S, k, θ, A_s, t) , p has a maximum for a particular τ_w . The fact that p has a maximum can be understood as follows: with the above parameters fixed, for very small τ_w the gas quickly desorbs from the walls and is removed so that little is left after t seconds; at the other extreme for very large τ_w even though little of the gas

has desorbed from the walls in the t seconds p is again very small since $p \propto 1/\tau_w$ (equation 3). Thus for some τ_w between these two limits the pressure attains a maximum value.

III. The Maximum Pressure

It is apparent from either Eq. 3 or Fig. 3 that considerably more information is necessary to find $p(t)$ than is a priori available even under the simple assumption that only a single state is present at $t = 0$. However it is fairly well-known from adsorption-desorption studies⁷ that only $\sim 10^{15}$ molecules/cm² of a volatile gas are able to be adsorbed at room temperature in a single state on any particular surface. This observation applies not only to the adsorption of gases on metal surfaces but also to the adsorption of alkali metals on metal and semiconducting surfaces.⁸ It thus appears that the phenomenon of a maximum of $\sim$ monolayer adsorption on surfaces by volatile materials is general and has been recognized for a number of years. Thus although the initial concentration of the particular adsorbed species which limits the pressure t seconds after the pumping has started is not known in detail, the above evidence indicates that it should be less than $\sim 1 - 2 \times 10^{15}$ /cm² of real surface area.⁹

The sojourn time of the adsorbed species is still not known at this point. However after fixing the various parameters (S, t, k, θ) the sojourn time is chosen to be the worst possible

(see Fig. 3). This is accomplished by setting $\left. \frac{\partial p}{\partial t} \right|_{t=\tau_w^0}$ to zero and evaluating $p(t)$ at τ_w^0 . An expression is obtained in this manner for a quantity, $P_{\max}$, which should be larger than the measured pressure at time t given that $\theta \times 10^{15}$ molecules/cm² are initially adsorbed in the worst possible state on the surface, a result independent of the actual sojourn time of the adsorbed species. The resulting expression for $P_{\max}$ is:

$$P_{\max} = 1.146 \times 10^{-5} \frac{\theta A}{St} \left\{ 1 + \frac{(2+k)}{(1+k)} \frac{\tau_s}{t} + O(\varepsilon^2) \right\} \text{ torr} \quad (4)$$

where

$$\varepsilon = \frac{\tau_s (1+k)}{t}$$

and τ_w^0 is found to be:

$$\tau_w^0 = \frac{t}{(1+k)} \left\{ 1 - \frac{2\tau_s}{t} + O(\varepsilon^2) \right\} \quad (5)$$

$n_w(t, \tau_w^0)$ may also be evaluated and is given by:

$$n_w(t, \tau_w^0) = \frac{n_w(0)}{e} [1 + O(\varepsilon)] \quad (6)$$

As indicated by Eq. 4, $P_{\max}$ depends only very weakly on k and in fact k need not be known for $P_{\max}$ to be accurately determined. It is interesting to consider that the pressure limitation during a pumpdown due to an adsorbed species is not necessarily due to a high wall pumping speed for the species. For example even a species for which $k \approx 0$ can limit the pressure in exactly the same manner as a species for which $k \sim 10^3 - 10^4$ (a different τ_w^0 will be necessary for these two cases).

A comparison between $P_{\max}$ evaluated from Eq. 4 and $P_{\max}$ determined numerically from the exact solution of $p(t)$ is shown in Fig. 4. Adequate agreement is found between the two solutions even for times as small as 10 seconds. For longer times there is negligible deviation between the two solutions.

Thus summarizing the above discussion, Eq. 4 is expected to provide for $\theta \approx 1$ a reasonably accurate estimate for the value the pressure should be strictly less than t seconds after the pumping has started, given that the pressure in the system is due to an adsorbed surface phase.

IV. Experimental Test

It was decided to test the above limit statement in a system in which as many of the parameters as possible could be controlled. The experimental system consisted of a 5.1 l volume with a geometric wall area of 2067 cm² of which 870 cm² were aluminum, the remainder being stainless steel. Onto this was placed a $\sim 10^3$ l/s liquid helium cryopump which was connected to the system through a bakeable valve which when appropriately opened had a measured N_2 conductance of 19.6 l/s. Into the volume were placed an ionization gauge and a UTI mass spectrometer. The stainless steel and aluminum sections were chemically cleaned and smoothed to remove the oxides and reduce the surface areas of the materials. The system was assembled and baked under vacuum for ~ 20 hours at 200 C. When cooled to room temperature the N_2 equivalent pressure was $2 - 4 \times 10^{-10}$ torr (when the conductance to the

cryopump was 19.6 l/s) which represents the magnitude of the diffusion contribution to the total pressure. After the bake and with the system at room temperature the cryopump was valved off and the system exposed to the atmosphere (at 760 torr) for 1 hour. The system was then pumped with a trapped mechanical pump for 5 minutes, for 10 minutes with a LN_2 cooled vac-sorb pump. Fifteen minutes after the end of the exposure the cryopump valve was opened and all other pumps valved off; ten minutes later the ion gauges were turned on and 5 minutes later the first pressure reading was made. The pressure was then recorded for the succeeding ~ 6 days. It should be mentioned that all times noted in the figures refer to the end of the exposure (the start of the mechanical pumping).

The entire sequence of bake plus cooling to room temperature plus atmospheric exposure and subsequent pumpdown was performed two times without the mass spectrometer operating and a third time with both the ion gauge and mass spectrometer in operation. Figure 5 shows the gas composition during the third pumpdown agreeing qualitatively with the observations of other investigators.¹⁰ It should be noted that the mass spectrometer sensitivity was determined by a comparison with the ionization gauge for various gases (H_2 , N_2 , Ar, CH_4) before the start of the experiment and thus has a precision of $\sim 20\%$ for any particular gas.

Figure 6 shows the pressure during the third trial measured two ways and indicates that the mass spectrometer was not perturbing the system gas pressure during the measurements. The darkened rectangle in the lower right hand corner of Fig. 6 is a deduction of the N_2 equivalent pressure from the appropriately weighted sum of partial pressures again indicating that the N_2 equivalent pressure with the mass spectrometer off was the same as that with the mass spectrometer on. The implication of the above is that neither the mass spectrometer nor the ion gauge were perturbing the pressure measurements during pumpdown.

Using the data presented in Fig. 5, the total number of molecules desorbed vs. time (from 1.7×10^3 seconds) can be determined and is shown in Fig. 7. The data is normalized to the geometric area A and indicates that a total of $\sim 3 \times 10^{15}$ molecules/cm² desorb during the entire pumpdown and is in accord with our previous estimate in Sect. III concerning the amount of gas initially adsorbed on a surface. It should be noted that this result is also in agreement with other investigations.¹⁰

Figure 8 presents the data acquired during the three trials and is a plot of the nitrogen equivalent pressure in the system vs. time from the end of the 1 hour exposure. Also given in Fig. 8 is $P_{\max}$ from Eq. 4. To estimate the real area used in Eq. 4 from the geometric area a factor of 1.5 was used. The choice of this was somewhat arbitrary but probably represents the minimum factor one can assume. Seen in this figure is that $P_{\max}$ provides an upper bound to the pumpdown pressure and in fact a reasonable estimate

(within a factor of 3) of the system pressure as a function of time from 10^3 - 10^6 seconds. Although it should be clear from the preceding discussion a number of system parameters have not been necessary to be included in the estimation of $P_{\max}$; namely, the wall temperature, the exposure gas composition and the wall material.⁴ Thus a system with a different set of parameters (i.e. a hotter or colder wall temperature) is expected to have at any time t a pressure less than $P_{\max}$. It may be worthwhile to emphasize that in general $P_{\max}$ is expected to provide only an upper bound to the pumpdown pressure and not necessarily an estimate of this pressure. The fact that in the present situation the measured and $P_{\max}$ values were approximately the same indicates that there were $\sim$ monolayer amounts of a surface species present with the most inappropriate τ_w, k combinations. Said slightly differently, the pressure couldn't have been much worse at any time in the entire pumpdown cycle.

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References

1. P. A. Redhead, J. P. Hobson, E. V. Kornelsen, The Physical Basis of Ultra-High Vacuum, Chapman and Hall Ltd., London, 1968.
2. J. P. Hobson, Trans. 8th AVS Vacuum Symp. (Pergamon Press, New York, 1962).
3. D. G. Bills, J. Vac. Sci., Technol. 6, 166 (1969).
4. Assuming that wall materials of equivalent real surface areas are chosen.
5. The symbol $O(\delta^2)$ means terms of the order of δ^2 are neglected in the sum.
6. It is interesting to note that the only parameter not needed is the system volume.
7. S. M. Ko and L. D. Schmidt, Surf. Sci 47, 557 (1975); P. A. Redhead, Trans. Far. Soc. 57, 641 (1961) and the references therein.
8. The initial concept of monolayer adsorption dates back at least to the work of J. B. Taylor and I. Langmir, Phys. Rev. 44, 423 (1933). More recently studies of the adsorption of alkali's on semi-conducting crystals also indicating monolayer type adsorption have been made by Peria and co-workers. See for example the thesis of R. E. Ericson, University of Minnesota, 1974 and the included references to earlier work.

9. This conclusion has also been reached by Hobson in Ref. 2.
10. Yale Strausser, Technical Report VR-51, Varian Associates, Palo Alto, Calif., 1969.

FIGURE CAPTIONS

1. Figure 1 shows a schematic of the vacuum system considered.
The elements are: volume V (liters) pumping speed S (liter/s),
wall pumping speed S_w (liter/s), a real leak L (torr liter/s),
and a wall outgassing rate q_w (torr liter/s). Neg. #5-1141-76
2. Figure 2 shows the pressure as a function of time for a fixed
sojourn time but several wall pumping speeds. Neg. #5-1137-76
3. Figure 3 is a plot of $pS(1+k)/\theta A_s$ as a function of τ_w for
various $t/(1+k)$. The solution for E/KT_w was found by taking
 $T_w = 300$ K, $\gamma = 10^{13}$ /s. Neg. #5-1139-76
4. Figure 4 shows $P_{\max}$ numerically calculated from the exact
solution of $p(t)$ and compared with Eq. 4. Neg. #5-1142-76
5. Figure 5 gives the partial pressures of the various gases during
a pumpdown from an atmospheric exposure. Seen is that H_2O dominates
the spectrum for the first few days but is also superlinear in
its decay whereas CO is sublinear and eventually overtakes the
 H_2O partial pressure. Neg. #5-1138-76
6. Figure 6 shows the nitrogen equivalent pressure together with the
sum of the partial pressures during a pumpdown. Neg. #5-1136-76
7. In Figure 7 is shown the molecules desorbed/cm² during a pumpdown
derived from the data given in Figure 5. Neg. #5-1135-76

8. The nitrogen equivalent pressure plotted as a function of time from the start of pumping after a 1 hour atmospheric exposure for the three trials. Shown also is $P_{\max}$ given by Eq. 4.

Neg. #5-1144-76