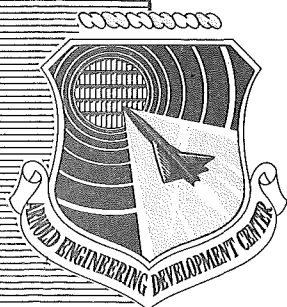


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ANALYSIS OF METHODS FOR DETERMINING OUTGASSING RATES

By

J. I. Shipp and J. D. Trolinger
Experimental Research Group
Office of the Chief Scientist
ARO, Inc.

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Errata AEDC-TDR-64-180*, December 1964

Please note the following revisions:

Last paragraph, page 1 is corrected to read:

When a substance is placed in a gaseous environment, it is continuously struck by fast-moving gaseous molecules. These gaseous molecules may either rebound or they may be trapped upon striking the surface of the material. When a particle strikes a surface and is retained by the surface, it is said to be adsorbed. Furthermore, the adsorbed gas may enter the interior of the solid by diffusion or injection; such molecules are said to be absorbed. The exact nature of the mechanism is often difficult to ascertain quantitatively and since both processes may occur simultaneously it is convenient to apply a separate term, sorption, to the trapping of the gaseous molecules by either or both processes. The molecules that are sorbed remain in thermal-motion; however, they can gain sufficient energy to escape the surface of the material. This process is basically termed desorption.

Equation 2, page 4 should read:

$$F_1 = C(P_1 - P_2)$$

instead of

$$F_1 = C(P_2 - P_1)$$

Equation 9, page 5: Last term on righthand side should read:

$$C(P_1 - P_2)$$

*J. I. Shipp and J. D. Trolinger. "Analysis of Methods for Determining Outgassing Rates." Arnold Engineering Development Center, Arnold Air Force Station, Tennessee. AEDC-TDR-64-180, December 1964. (Unclassified Report).

UNCLASSIFIED

Equation 11, page 5: Last term on righthand side should read:

$$\frac{S_p C}{S_p + C} P_1 + G_c - L_c$$

Equation 20, page 7 should read:

$$+G_s(t) =$$

instead of

$$-G_s(t) =$$

Equation 21, page 8 should read:

$$-G_s(t) = S_p [P_3(t) - P_{3e}(t)]$$

Equation 26, page 9 should read:

$$\frac{dN}{dt} = b \left(1 - \frac{N}{N_s} \right) n - cN$$

Equation 31, page 10 should read:

$$\frac{dN}{dt} = \frac{-b}{S_p} \left(1 - \frac{N}{N_s} \right) \frac{dN}{dt} - cN$$

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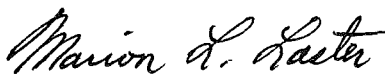
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ABSTRACT

Methods of determining outgassing rates of materials under vacuum are discussed with emphasis on the accuracy and limitations of each. Pressure measurement techniques included are rate of evacuation, rate of rise, and a number of conductance methods. Assuming Langmuir's model for sticking probability, it is shown that these techniques can introduce large errors in determinations of desorption rates due to incorrect choice of pumping speed. Instrument calibration procedures and comparisons of results employing different techniques are also given.

PUBLICATION REVIEW

This report has been reviewed and publication is approved.



Marion L. Laster
Aerospace Engineer
Propulsion Division
DCS/Research


Donald R. Eastman, Jr.
DCS/Research

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NOMENCLATURE

A	Adsorption rate
a	Area of sample
b	$1/4 \bar{V} f_0 a$
C	Conductance
c	$KT/h e^{-E/KT}$
D	Desorption rate
E	Activation energy for desorption
e	Natural logarithm base
F	Flow rate
F_{1i}	Flow rate of i^{th} gas through conductance
F_{1e}	Flow rate without sample
F_1	Flow rate through conductance
F_2	Diffusion pump throughput
f	Sticking probability
f_i	Mole fraction
f_0	Clean surface sticking probability
G_C	Virtual leak rate of Chamber 1
G_{C2}	Virtual leak rate of Chamber 2
G_{Ci}	Virtual leak rate of i^{th} gas in Chamber 1
G_S	Outgassing rate of sample
G_{Si}	Outgassing rate of i^{th} gas from sample
h	Planck's constant
i	Mass spectrometer collection current
K	Boltzmann's constant
L_C	Real leak rate of Chamber 1
L_{Ci}	Real leak rate of i^{th} gas in Chamber 1
L_{C2}	Real leak rate of Chamber 2
L_S	Standard leak rate
L_t	Total leak rate (real and virtual) for Chambers 1 and 2

N	Number of adsorbed particles
N_0	Number of adsorbed particles initially
N_s	Number of adsorbed particles at saturation
n	Number of gas molecules per unit volume
P	Pressure
P_i	Partial pressure of i^{th} gas
P_1	Pressure in Chamber 1
P_2	Pressure in Chamber 2
P_3	Pressure at diffusion pump inlet
$P_{3\text{base}}$	Base pressure at the diffusion pump inlet
r	Sensitivity of ion gage to composite gas
r_i	Sensitivity of ion gage to i^{th} gas
S	Pumping speed
S_1	Pumping speed from chamber 1
S_p	Pumping speed of pump
T	Absolute temperature of gas
T_s	Absolute temperature of surface
t	Time
\bar{U}	Average velocity of gas molecules
V	Volume
V_1	Volume of Chamber 1
V_2	Volume of Chamber 2
X	N/N_s
Y	Radius of conductance
Z	Length
α	Ratio of "partial" pressure to mass spectrometer collection current
η	Viscosity of gas

1.0 INTRODUCTION

In a recent test program at the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), one of the test objectives was to determine the rate and composition of gases evolving from a test article in a pressure simulated flight trajectory (Ref. 1). During the planning phase it was necessary to select a technique whereby gas flow rates emanating from the test article could be determined. The literature was searched for standard methods of determining the composition and the rate of outgassing of various materials in a high vacuum environment. Upon evaluation of the methods that were reported in the literature, it was learned that no single method could be recognized as standard by vacuum technologists, and furthermore, every method had distinct advantages. However, subtle limitations inherently existed for each technique which, if not recognized, could result in errors even on the orders of magnitude. Despite the fact that the methods in the literature were quite similar, they did require modification for application to the test program.

A very important by-product in attaining the test objective was therefore a summary and analysis of outgassing rate measuring techniques. The purpose of this report is to present a summary of the conventional techniques for determining outgassing rates and to discuss their advantages and limitations. To minimize the amount of supplementary reference material that is required, some of the basic equations pertinent to evaluating outgassing rate measuring techniques are developed.

2.0 DEFINITION OF TERMS

A discussion of the basic processes inherent with material outgassing and methods of measurement may be clarified by discussing some of the important fundamental physical processes that take place. The purpose of this section is therefore to present qualitative descriptions of outgassing, adsorption, absorption, desorption, and sublimation.

When a substance is placed in a gaseous environment, it is continuously struck by fast-moving gaseous molecules. These gaseous molecules may either rebound upon striking a surface or they may be trapped on the surface of the material. Two basic processes can occur when a

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particle strikes a surface and is retained by the surface: (1) The gas may either interact and remain on the surface by virtue of polarization or chemical reactions, or (2) it may be adsorbed. Furthermore, the adsorbed gas may enter the interior of the solid by diffusion or injection; such molecules are said to be absorbed. The exact nature of the mechanism is often difficult to ascertain quantitatively and since both processes may occur simultaneously it is convenient to apply a separate term, sorption, to the trapping of the gaseous molecules by either or both processes. The molecules that are sorbed may remain in thermal motion; however, they can gain sufficient energy to escape the surface of the solid. This process is basically termed desorption.

The desorption rate is found to be an increasing function of the number of gaseous molecules sorbed and since the surface ultimately becomes saturated with gas molecules, an equilibrium condition, where the sorption rate is equal to the desorption rate, is finally attained at a given temperature and pressure.

Sublimation is another mechanism by which molecules of a substance may escape from a material into its environment. However, for most substances whose desorption rates are of practical interest, the sublimation rate may be considered negligible. In any event, the same measuring techniques may be applied.

At any given pressure, regardless of the mechanism governing the rate processes, the outgassing rate of a substance will herein be defined as the time rate of change of sorbed and bound molecules. Therefore, even though sorption, desorption, and sublimation rates may be large, the outgassing rate of a substance in equilibrium with its environment is considered to be zero.

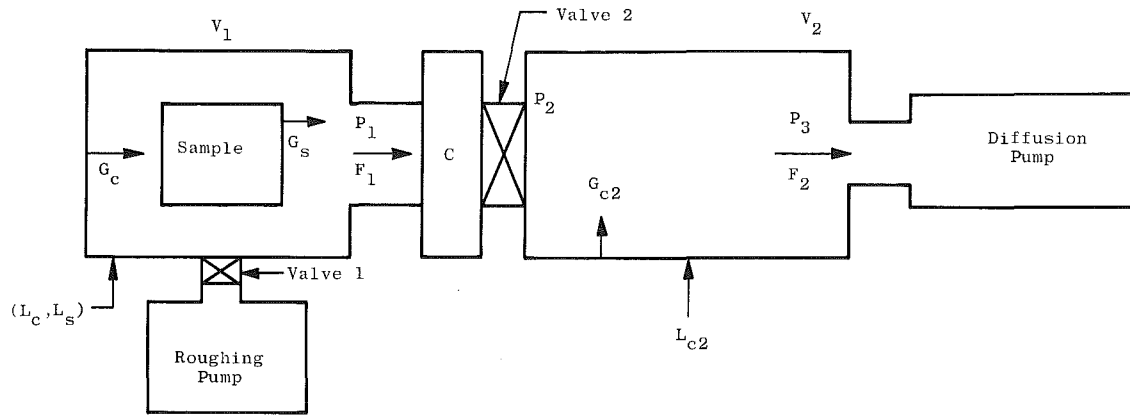
Another important requirement for outgassing data to be useful is that it must be either collected in an environment similar to where it is later to be applied (for example, outgassing rate measurements during a simulated pressure profile), or measurements which are altogether independent of the sample environment must be made (measuring the desorption rate). In the latter case, free outgassing is a term commonly used instead of desorption. Free outgassing occurs only when the sorption rate is zero.

3.0 DETERMINING OUTGASSING RATES BY PRESSURE MEASUREMENTS

Techniques employed for determining outgassing rates can be divided into two classes. One class involves determination of gas flow rates from

a sample by various pressure monitoring techniques; the other involves sample weight loss measurements. The first method is the most widely applicable and will be presented in detail in this section. The second is the only direct means for measuring outgassing rates but is limited in applicability and will only be briefly discussed.

Four methods have been employed extensively to determine the outgassing rates by pressure measurements. Each of these methods resorts to a simple application of the continuity equation which is the statement of the conservation of particles. Consider a vacuum system of the type shown in Sketch 1.



Sketch 1

A typical data run might proceed in the following manner: At $t = 0$ a roughing pump or sump tank opens to V_1 , reducing its pressure to the tens of micron range. The valve is then opened connecting V_1 to V_2 which has already been pumped to its base pressure. P_1 is then reduced, in a short time, to a pressure at which meaningful data can be taken. (The system of the Experimental Research Group can attain a pressure below 10^{-5} torr from 760 torr in less than 100 sec.) According to the exact geometry chosen, one or more of the pressures is then monitored and this leads ultimately to the sample outgassing rate.

3.1 CONDUCTANCE METHODS

The continuity equation for volume 1 is

$$V_1 \frac{dP_1}{dt} = -G_s - G_c + L_c - F_1 \quad (1)$$

Therefore, to determine G_s from Eq. (1), $V_1 dP_1/dt$, G_c , L_c , and F_1 must be measured. The determination of F_1 by measuring the pressure difference across the conductance is now considered.

By definition of conductance,

$$F_1 = C (P_2 - P_1) \quad (2)$$

Where C is

- a) a function of geometry and gas temperature for free molecular flow
- b) a function of geometry, gas temperature, P_1 and P_2 for viscous flow
- c) not amenable to theoretical analysis for the transitional regime between a and b.

Determinations of F_1 can therefore be accomplished by selecting particular types of conductances, monitoring P_1 and P_2 , and applying Eq. (2). Table 1 gives the value of the conductance for a number of geometries which might be used in an experimental apparatus.

3.2 RATE OF RISE METHOD

It is possible to determine outgassing rates without conductances. One way of doing this is called the rate of rise method. If, during the pumpdown of a system, valves V_1 and V_2 are closed, isolating chamber one, the flow rate F_1 is eliminated and Eq. (1) becomes

$$-G_s = V_1 \frac{dP_1}{dt} + G_c - L_c \quad (3)$$

If G_c and L_c can be determined or made negligible, G_s can be determined by monitoring P_1 . The chamber leak rate, L_c , can be determined as will be shown in Section 3.5; however, the determination of the chamber outgassing rates, G_c , becomes inherently more difficult than is described in Section 3.6 for it varies with chamber pressure and may even take on positive values. Under this condition (positive outgassing rate) the chamber walls are adsorbing a net amount of gas (adsorption pumping). This phenomenon, as related to outgassing measurements, was studied experimentally in Ref. 2 (See Section 5.2).

3.3 EVACUATION RATE METHOD

Another technique for determining outgassing rate, without considering the conductance, is the evacuation rate method (Ref. 3). The

continuity equation for volume two is

$$V_2 \frac{dP_2}{dt} = F_1 - F_2 - G_{c2} + L_{c2} \quad (4)$$

Substituting for F_1 Eq. (1) yields

$$V_2 \frac{dP_2}{dt} = -V_1 \frac{dP_1}{dt} - G_s - G_c - G_{c2} + L_c + L_{c2} - F_2 \quad (5)$$

The diffusion pump throughput, F_2 , can be determined by monitoring P_2 and using diffusion pump calibration data. The throughput into an ordinary diffusion pump is a function of only the inlet pressure and is given over a wide range by the product of a constant, called the pumping speed of the pump, and the inlet pressure. The calibration procedure for determining pumping speed is covered in Section 3.5.

3.4 SIMPLIFYING CONSIDERATIONS

In all of the previous methods, the equations imply that one must compute the time derivatives of the pressure. Experimentally, this is usually unnecessary in all except the rate of rise method. This is true because the chamber pressure becomes numerically small after a short pumping time. Thereafter, large decreases in the pressure-time derivative are not experienced and thus, neglecting $V dP/dt$, Eq. (1) simplifies to

$$-G_s = F_1 + G_c - L_c \quad (6)$$

and Eq. (5) becomes

$$-G_s = F_2 + G_c + G_{c2} - L_c - L_{c2} \quad (7)$$

Extending the definition of pumping speed to any point where the pressure is P , the pumping speed, S , is defined as

$$S = \frac{F}{P} \quad (8)$$

and if G_{c2} , L_{c2} , and all pressure time derivatives are negligible, Eqs. (6) and (7) can be further simplified. In such a situation

$$F_2 = F_1 = S_p P_2 = S_1 P_1 = C(P_2 - P_1) \quad (9)$$

rearranging Eqs. (8) and (9) results in

$$\frac{1}{S_1} = \frac{1}{C} + \frac{1}{S_p} \quad (10)$$

Therefore

$$-G_s = S_1 P_1 + G_c - L_c = \frac{S_p C}{S_1 C} P_1 + G_c - L_c \quad (11)$$

If the vacuum system is well calibrated and the values of G_C and L_C are known, the outgassing rate of a sample can be determined by Eq. (11) by monitoring the single pressure, P_1 . Or the outgassing rate may be determined by monitoring pressure P_2 and using Eqs. (7) and (9), when the value of L_t is known.

3.5 LEAK RATE AND PUMPING SPEED OF A VACUUM SYSTEM

The pumping speed and the leak rate of a vacuum system can easily be determined by introducing an additional known leak rate into the system. The system is pumped to its base pressure and the flow through a standard leak initiated. When equilibrium is attained,

$$L_s + L_t = F_2 \quad (12)$$

where

$$L_t = -G_{C2} - G_C + L_C + L_{C2} \quad (13)$$

The term $-(G_{C2} + G_C)$ is known as the virtual leak rate and includes back diffusion rate from the diffusion pump, chamber outgassing rate, and any other sources of gas in the chamber. The sum $L_C + L_{C2} + L_s$ is called the real chamber leak rate and is the rate of gas flowing from the outside of the chamber. The throughput to the diffusion pump is given by (assuming a single species of gas)

$$F_2 = S_p P_3 \quad (14)$$

Substituting for F_2 (Eq. 12), it is found that

$$\frac{L_t + L_s}{P_3} = S_p \quad (15)$$

A known standard is selected such that initially

$$L_s \gg L_t \text{ implying } P_3 \gg P_{3 \text{ base}} \quad (16)$$

hence

$$S_p \approx \frac{L_s}{P_3} \quad (17)$$

The leak rate and pumping speed may also be obtained by taking a number of data points for decreasing L_s . A plot of L_s versus P_3 should yield, Eq. (15), a straight line with a slope $1/S_p$ and an intercept L_t/S_p . Thus, the pumping speed as well as the total leak rate of the system is obtained. The assumption made in employing the value of L_t obtained in this manner is that G_{C2} and G_C remain essentially constant or that they are negligible compared to L_C .

The real leak rate of a high vacuum system is generally independent of the internal pressure and for a carefully designed apparatus remains

constant for extended periods of time. In tests conducted at AEDC, the chamber leak rate was found to be constant by monitoring the system in the following manner: A plastic bag was placed around the external periphery of the test chamber and was inflated with helium. A sensitive mass spectrometer was employed to determine the helium content in the cell and thus changes in helium background would indicate a change in leak rate, assuming helium is not among the outgassing constituents.

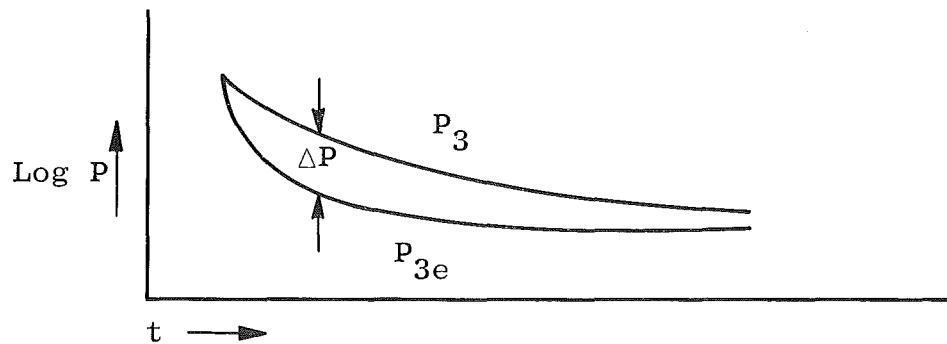
3.6 CHAMBER OUTGASSING RATE

The simplest way to account for chamber outgassing rate is to design the chamber such that G_C is either negligible or nearly constant when outgassing measurements are made. If it is constant, then the outgassing rate is included in the value of the total leak rate (which includes virtual leak rate). The usual technique for determining the time dependency of G_C is as follows:

The empty system is pumped to its base pressure. After dp/dt becomes negligible, the equation for the calibration pumpdown is:

$$F_{2e}(t) = S_p P_{3e}(t) = L_t(t) \quad (18)$$

Thus $L_t(t)$ is known as a function of time, and assuming that the leak rate does not change with the sample inserted (Eq. 18), Eqs. (6) or (7) can then be solved. The pressure versus time curves for an empty pumpdown and a sample pumpdown are usually plotted one over the other to facilitate data reduction as shown in the following figure (Sketch 2).



Sketch 2

Using Eq. (6) with Sketch 2

$$-G_s(t) = F_1(t) - F_{1e}(t) \quad (19)$$

which reduces to

$$+G_s(t) = C P_3(t) - P_1(t) - P_{2e}(t) - P_{1e}(t) \quad (20)$$

and Eq. (7) becomes

$$-G_s(t) = S_p [P_s(t) - P_{se}(t)] \quad (21)$$

A number of studies, by this group and at other laboratories, have shown conclusively that the pumpdown time for a vacuum system can be reduced considerably by the proper conditioning; that is, the chamber outgassing rates are reduced in a shorter time if the chamber is conditioned before pumpdown. A very successful conditioning procedure developed in Ref. 1 is the following: The cell is pumped to its base pressure and left there for twenty-four hours. It is then bled back to atmosphere with a dry gas such as nitrogen or a noble gas. Short exposures to atmospheric air (up to two hours) do not substantially erase the beneficial characteristics resulting from this conditioning. In no case should a vacuum cell be bled from vacuum with anything but dry gas. There is little need to emphasize the undesirable effects of water vapor on pumpdown time.

4.0 OUTGASSING RATE DETERMINATION BY WEIGHT LOSS METHOD

The only direct means for measuring outgassing rate, presently found in application, is where a microbalance is enclosed in a vacuum chamber and the weight loss of a sample, caused by its outgassing, is measured (Ref. 4). The limitations imposed by sample weight are obvious. However, this technique does offer many advantages over pressure measurement methods. A weighing system permits varying the temperature of the sample and requires no accurate pressure measurement. For samples of thin foils or fine particles with a large surface-to-volume ratio, and for samples where appreciable gas diffusion into the interior occurs so that a measurable percentage of weight loss attributable to outgassing occurs, this technique appears to be unique.

5.0 LIMITATIONS IN DETERMINATION OF OUTGASSING RATES

There are two major types of errors and limitations inherent in measuring outgassing rates. One is caused by the inability of the system to produce free outgassing when it does not sufficiently remove residual gas particles which may be adsorbed by the sample. The second type of error is caused by inaccuracies in measurements even though free outgassing is occurring; these errors include instrument errors as well as other errors such as the uncertainty of the real and virtual leak rate of the system.

5.1 PUMPING SPEED REQUIREMENTS FOR FREE OUTGASSING RATE

Since the net outgassing rate (adsorption minus desorption) depends upon the vacuum system in which the measurement is to be made, it is of general interest to develop criteria which allow free outgassing or pure desorption rates to be determined. In the following, a single species of outgassing constituent is assumed for simplicity. The extension to several different gases is straightforward.

The outgassing rate is given by

$$\frac{dN}{dt} = A - D \quad (22)$$

The second term on the right of Eq. (22) can be derived from a simplified kinetic ejection model (Ref. 5). The result is, assuming a homogeneous surface (neglecting diffusion)

$$D = \frac{NkT}{h} e^{-E/kT} = cN \quad (23)$$

The adsorption term is obtained from the kinetic theory of gases (Ref. 6). Multiplying the number of particles striking the test sample per unit time by f , the probability of sticking, yields

$$A = 1/4 n \bar{U} f a \quad (24)$$

The sticking fraction, f , is known to increase as the number of adatoms decreases and has been found to be of the order of unity for a clean surface for many materials (Ref. 7). Langmuir's theory of adsorption (Ref. 8) postulated the following

$$f = f_0 \left(1 - \frac{N}{N_s} \right) \quad (25)$$

where f_0 is the clean surface sticking probability. In the following development this same model is adopted. This assumption implies that the probability of sticking is proportional to the number of available adsorption sites. If dissociation of a diatomic molecule accompanies adsorption, two adjacent adsorption sites would be necessary and the sticking probability would become proportional to the square of the right side of Eq. (25).

Disregarding dissociation, the outgassing rate from Eq. (22) becomes

$$\frac{dN}{dt} = b \left(1 - \frac{N}{N_s} \right) n - cN \quad (26)$$

where $b = 1/4 \bar{U} f_{0a}$. A second equation involving n and N may be written from particle conservation. Neglecting real and virtual leaks of the system

$$-k T_s \frac{dN}{dt} = S_p P + V \frac{dP}{dt} \quad (27)$$

From the ideal gas law

$$P = nkT \quad (28)$$

or

$$\frac{dP}{dt} = kT \frac{dn}{dt} \quad (29)$$

Assuming T_s is equal to the gas temperature, Eq. (27) becomes

$$\frac{dN}{dt} = -S_p n - V \frac{dn}{dt} \quad (30)$$

Eqs. (26) and (30) comprise two simultaneous equations in n and N ; the former is seen to be non-linear. Neglecting $V \frac{dn}{dt}$ in Eq. (30) (see Section 3.4) solving for n , and substituting into Eq. (26) yields

$$\frac{dN}{dt} = \frac{-b}{S_p} \left(1 - \frac{N}{N_s} \right) \frac{dN}{dt} - cN \quad (31)$$

Normalizing Eq. (31) by dividing by N_s gives

$$\frac{dX}{dt} = \frac{-b}{S_p} (1 - X) \frac{dX}{dt} - cX \quad (32)$$

where

$$X = \frac{N}{N_s}$$

Equation (32) becomes

$$\frac{dX}{dt} = \frac{-c}{\frac{1 + b/S_p}{X} - \frac{b}{S_p}} \quad (33)$$

Note that the free outgassing rate may be obtained from Eq. (31) by setting the adsorption term equal to zero. Thus

$$\left(\frac{dN}{dt} \right)_{free} = -cN \quad (34)$$

Integrating Eq. (34) gives

$$N_{free} = N_0 e^{-ct} \quad (35)$$

Thus, free outgassing rate for this model is

$$\left(\frac{dN}{dt} \right)_{free} = cN_0 e^{-ct} \quad \text{or} \quad \left(\frac{dX}{dt} \right)_{free} = -c e^{-ct} \quad (36)$$

Figure 1 is a comparison of outgassing rates versus time for various values of b/S_p . The constant c appears on the ordinate and the abscissa to eliminate the necessity of a second parameter. Thus the ordinate is proportional to the log of the outgassing rate and the abscissa is plotted as time constants of the free outgassing rate (see Eq. 36). The initial condition for X was chosen to be unity, which assumes that at the time $V \frac{dN}{dt}$ becomes negligible ($t = 0$) the number on the surface is still N_s .

Another initial condition would not greatly affect the results, however. Note that initially the free outgassing rate ($b/S = 0$) is higher than any other, except at time $t = 0$ when all are equal. This is expected since the adsorption term initially is zero and increases faster for smaller pumping speeds (larger b/S). However, at some later time, crossovers occur. This is attributed to the fact that free outgassing rate depends directly on the number of atoms remaining on the surface and therefore decays faster.

Dayton (Ref. 9) has suggested that free outgassing could accurately be determined with pumping speeds of only a few tenths of a liter per sec for a sample with several sq cm of surface area. Equation (36) indicates that this statement is somewhat in error. The free surface sticking fraction has been shown to be of the order of unity (Ref. 7) for most materials at room temperature. The value of \bar{U} for air is approximately 4×10^4 cm/sec which gives $\frac{b}{a} \approx 10$ liters/sec/cm². For a pumping speed of 0.5 liters/sec, b/S_p is approximately 20 per unit sample area. Figure 1 emphasizes the magnitude of the error inherent in free outgassing measurements obtained by employing such a system. Assuming that $b/S_p = 0.1$ is sufficient to support free outgassing accurately, S_p should be approximately 100 liters/sec for each sq cm of sample area.

The results obtained above are for the rate of evacuation method; however, a similar development applies to the conductance methods where the pumping speed S_p is replaced by S_1 given by

$$\frac{1}{S_1} = \frac{1}{C} + \frac{1}{S_p} \quad (\text{See Section 3.4}) \quad (37)$$

Note that S_1 is smaller than either C or S_p ; hence, conductance methods of measuring free outgassing rate require larger S_p than the evacuation method.

Even though the model developed above is strictly valid only for samples which obey Langmuir adsorption theory, it serves to amplify the fact that systems with inadequate pumping speeds affect free outgassing rate measurements to the extent that much existing data may be greatly

in error. Without a zero external pressure, adsorption will take place. As the number of adsorbed atoms decreases, the sticking probability increases (this has been shown experimentally for most materials) and thus the importance of the adsorption term increases. Even at an external pressure of 10^{-6} torr at room temperature, approximately 3×10^{14} atoms strike a sq cm of surface per second. If the sticking fraction is large, obviously this number becomes significant.

5.2 ADDITIONAL LIMITATIONS OF THE RATE OF RISE METHOD

The limitations in determining the free outgassing rate caused by inadequate pumping speeds are common to all methods of measurements. However, two additional sources of error are introduced by the use of the rate of rise method. These are: (1) an increase in the importance of the adsorption by the sample caused by the increase in ambient pressure and (2) adsorption by the chamber caused by the ambient pressure increase. Even though these effects proceed by essentially the same mechanism they are distinct since equilibrium for each can occur at different times (Ref. 2). In fact, it is desirable that equilibrium for the chamber occur much faster than that of the sample (Section 3.6).

The first effect can be analyzed by employing the adsorption model introduced in Section 5.1. Neglecting effects of the chamber, the following equation can be written for the rate of rise [Eq. 30 ($S_p = 0$)].

$$\frac{dN}{dt} = -V \frac{dn}{dt} \quad (38)$$

For $N/N_s \ll 1$, Eq. (26) becomes, upon taking the derivative,

$$\frac{d^2N}{dt^2} = b \frac{dN}{dt} - c \frac{dN}{dt} \quad (39)$$

Using Eq. (38), Eq. (39) becomes

$$\frac{d^2N}{dt^2} = \frac{-b}{V} \frac{dN}{dt} - c \frac{dN}{dt} = \frac{-dN}{dt} \left(\frac{b}{V} + c \right) \quad (40)$$

Integrating Eq. (40) gives

$$\frac{dN}{dt} = \left(\frac{dN}{dt} \right)_0 e^{-\left(\frac{b}{V} + c \right) t} \quad (41)$$

where $\left(\frac{dN}{dt} \right)_0$ is the outgassing rate at the time that the pumping apparatus is valved from the system to begin the rate of rise. Thus, if the pumping

speed is sufficient to ensure free outgassing before the pump is valved off, Eq. (41) becomes

$$\frac{dN}{dt} = \left(\frac{dN}{dt} \right)_{free} e^{-b/Vt} \quad (42)$$

For a short rate of rise time $\left(\frac{dN}{dt} \right)_{free}$ is approximately a constant since c is small for most materials. Thus, to ensure accurate measurements using the rate of rise, V/b should be much greater than the time constant of the pressure measuring device to ensure that the pressure increase at time $t = 0$ can be followed by the sensing device. In this case

$$-v \left(\frac{dn}{dt} \right)_0 = (G_{free})_0 \quad (43)$$

If chamber adsorption becomes significant Eq. (38) will be altered by the pumping speed of the chamber walls. A discussion of this phenomenon can be found in Ref. 2.

5.3 INSTRUMENTATION CALIBRATION REQUIREMENTS

The fundamental instrument requirements for determining outgassing rates are devices to (1) measure the pressure-time profile, (2) establish the identity and quantity of outgassing products, and (3) detect and locate leaks (both real and virtual) in the system (See Section 3.5). Determining the correct system pressure is perhaps the major problem. Careful calibration procedures are necessary to obtain accurate data. Usually ion gages are calibrated against a McLeod gage using a dry noble gas, such as neon. Using this calibration, it is then possible to obtain calibrations for other gases from ion gage sensitivity factors given by Dushman (Ref. 10). These factors, r_i , are defined as the sensitivity* of a gage to a gas divided by its sensitivity to a calibration gas. By using mole fractions obtained from mass spectrometer data, these sensitivity factors should be weighted to give total gage sensitivity for the composite gas constituents for which the total pressure is desired.

$$\frac{1}{r} = \sum_i \frac{f_i}{r_i} \quad (44)$$

Thus pressure readings taken from a gage calibrated for a particular gas are divided by r to obtain total outgassing constituent pressure. Since

*Sensitivity of an ion pressure gage is defined as the ratio of the collection current to the pressure.

outgassing rates for various gases differ considerably, a continuous mass spectrometer scan should be used, and f_i obtained as a function of time so that a dynamic calibration can be made. These gage calibrations are important and often introduce large correction factors (Ref. 1).

Mass spectrometer calibration should be made as follows: The system under vacuum should be thoroughly purged with a dry noble gas, such as neon, several times and a liquid nitrogen trap temporarily cooled to remove condensable gases. When all but the neon mass peak becomes negligible, the calibration for neon can be obtained by employing a standard McLeod gage appended to the system (this results in a ratio, α , of pressure of neon per unit mass spectrometer collection current). Partial pressures of other gas constituents in the system during outgassing measurements are then obtained from

$$P_i = \frac{\alpha_i}{r_i} \quad (45)$$

and

$$f_i = \frac{P_i}{P} \quad (46)$$

Figure 2 is a comparison of total pressures of outgassing constituents consisting of various percentages of water vapor, nitrogen, oxygen, and hydrogen measured by a VG-1A ion gage, to the sum of the partial pressure measurements taken from a mass spectrometer. Calibration of both instruments was carried out as outlined above. The agreement between the two devices is seen to be satisfactory.

Dynamic gage response can contribute significantly to the measurement error when rapidly changing pressure conditions are encountered such as in rocket trajectory simulations (Ref. 1). Lagging response caused by enveloped gage (i. e., finite time for pressure impulse to flow through gage conductance, see Ref. 11), can be eliminated by the use of nude gages. However, ion gage electronic circuits also have finite response times and can also cause significant errors (Ref. 12).

5.4 SELECTIVE PUMPING

If the pumping unit for a vacuum system has a higher pumping speed for certain gases, every value of pumping speed must be known to determine correct flow rates. Even then, gas analysis data will be a function not only of the sample but of the pumping system and therefore are of little use in different systems. Almost any pumping system is selective to some extent, and analysis of gases evolving from a sample are always questionable unless a system is carefully calibrated to account for this effect.

To account for this effect, the theory presented in Section 3.4, Eq. (9) may be used and is generalized to give

$$F_{1i} = S_i P_i \quad (47)$$

which gives for the outgassing rate of the i^{th} gas

$$-G_{s i} = S_i P_i + G_{c i} - L_{c i} \quad (48)$$

6.0 COMPARISON OF METHODS

Outgassing measurements of an ion engine flight test package in a simulated launch trajectory were made (Ref. 1) using conductance, rate of rise, and rate of evacuation techniques. The system is shown schematically in Sketch 1 of Section 3.0. Typical outgassing data are shown in Fig. 3. It can be seen that the rate of rise method gave results much lower than those determinations by the other two methods. The errors involved in rate of rise measurements tend to yield values that are smaller than actuality. This is evidently the case in the data in Fig. 3. The rates measured by the evacuation rate technique and orifice conductance method were also substantiated by a flow measurement through the conductance C in Sketch 1.

7.0 SUMMARY AND CONCLUSIONS

An analysis of techniques for measuring outgassing rates has been presented, including rate of evacuation, rate of rise, and conductance methods. Two types of errors were shown to affect free outgassing determinations. These are the inability of the system to produce free outgassing conditions because of inadequate pumping speed and instrument errors coupled with system leak rate uncertainties. Results of experimentally determined outgassing rates using different techniques were compared. Requirements for a vacuum system in which free outgassing rate determinations can be made were established assuming a Langmuir adsorption model. From the foregoing study the following conclusions are drawn:

- (1) The rate of rise method for outgassing rate determination is the least accurate of those considered because of the inherent increase in ambient pressure.
- (2) Assuming the probability of adsorption is proportional to the number of available adsorption sites with the proportionality constant of the order of unity, it is shown that a pumping speed of the order of

100 liters/sec per sq cm of sample area is necessary to determine free outgassing rates accurately.

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TABLE 1
CONDUCTANCES OF VARIOUS GEOMETRIES¹

Geometry of Conductance	Free-Molecular Flow ²	Viscous Flow ³
Thin Orifice ⁴	$1/4n\bar{U}a$ (Note 5)	(Note 6)
Long Tube ⁷	$(2/3\pi)(r^3/Z)\bar{U}$ (Note 5)	$[(\pi Y^4)/(8\eta^2)] [(P_1 + P_2)/2]$ (Note 8)
Short Tube ⁹	$= \{1/[1 + (3/8)Z/Y]\} (a\bar{U}/4)$ (Note 10)	(Note 6)

1. It will be noted that conductance for free-molecular flow is dependent only on the geometry and the gas temperature, not on the pressure. This greatly simplifies calibration, for the conductance is usually constant. For viscous flow, calibration is complicated by the variation of conductance with pressure. Almost all equations given for conductances in transitional flow are empirical. Such equations are complicated and are of questionable accuracy. Therefore, it is advisable to avoid measurements in this regime.
2. Free-molecular flow occurs when the mean free path of a molecule is greater than the characteristic dimension of the conductance. The mean free path of air at 20°C is given by $\lambda = 5 \times 10^{-3}/P$ cm, where P is pressure in mm Hg. Therefore the requirement is $PY < 5\mu$ cm.
3. Viscous flow occurs when $\lambda \ll Y$ and the Reynolds number taken with the radius is less than 1200. For a circular pipe of radius Y, the flow is viscous if $F_1 < 4 \times 10^5 Y$, where F is the flow rate in micron liters per second and Y is the tube radius in cm. See Ref. 13, pp. 22-27.
4. The radius must be much greater than the length.
5. This relation requires also that the orifice diameter be much less than the dimensions of the chamber.
6. The conductance is a logarithmic function of pressure. See Ref. 10, pp. 111-116.
7. The length of the tube is much greater than its diameter.
8. This is the Poiseuille formula developed in Ref. 6. Conditions and assumptions are tabulated in Ref. 10, pp. 82-86.
9. The length is of the same order as the diameter.
10. Ref. 10, p. 91.

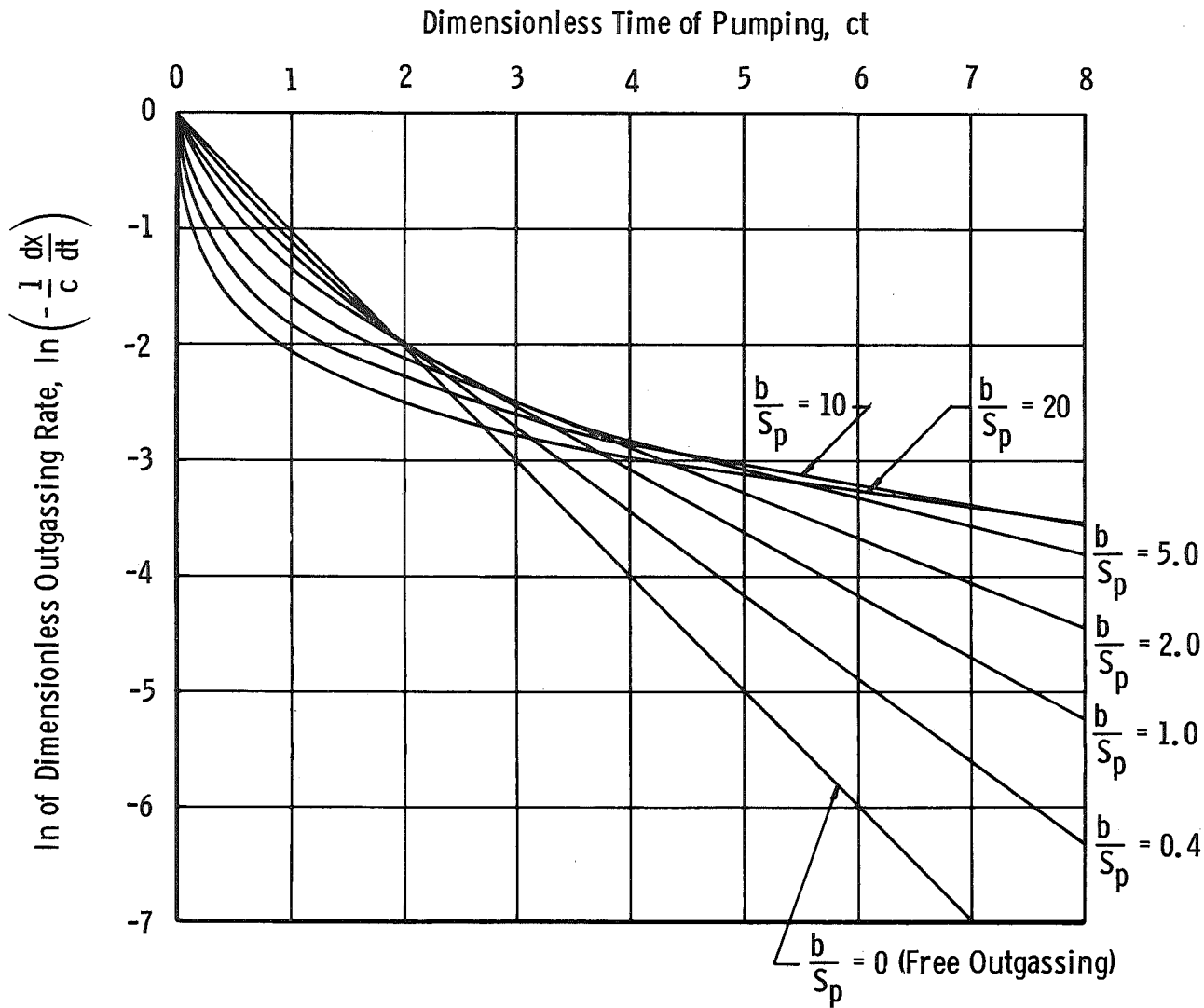


Fig. 1 Effect of Pumping Speed on Outgassing Rate

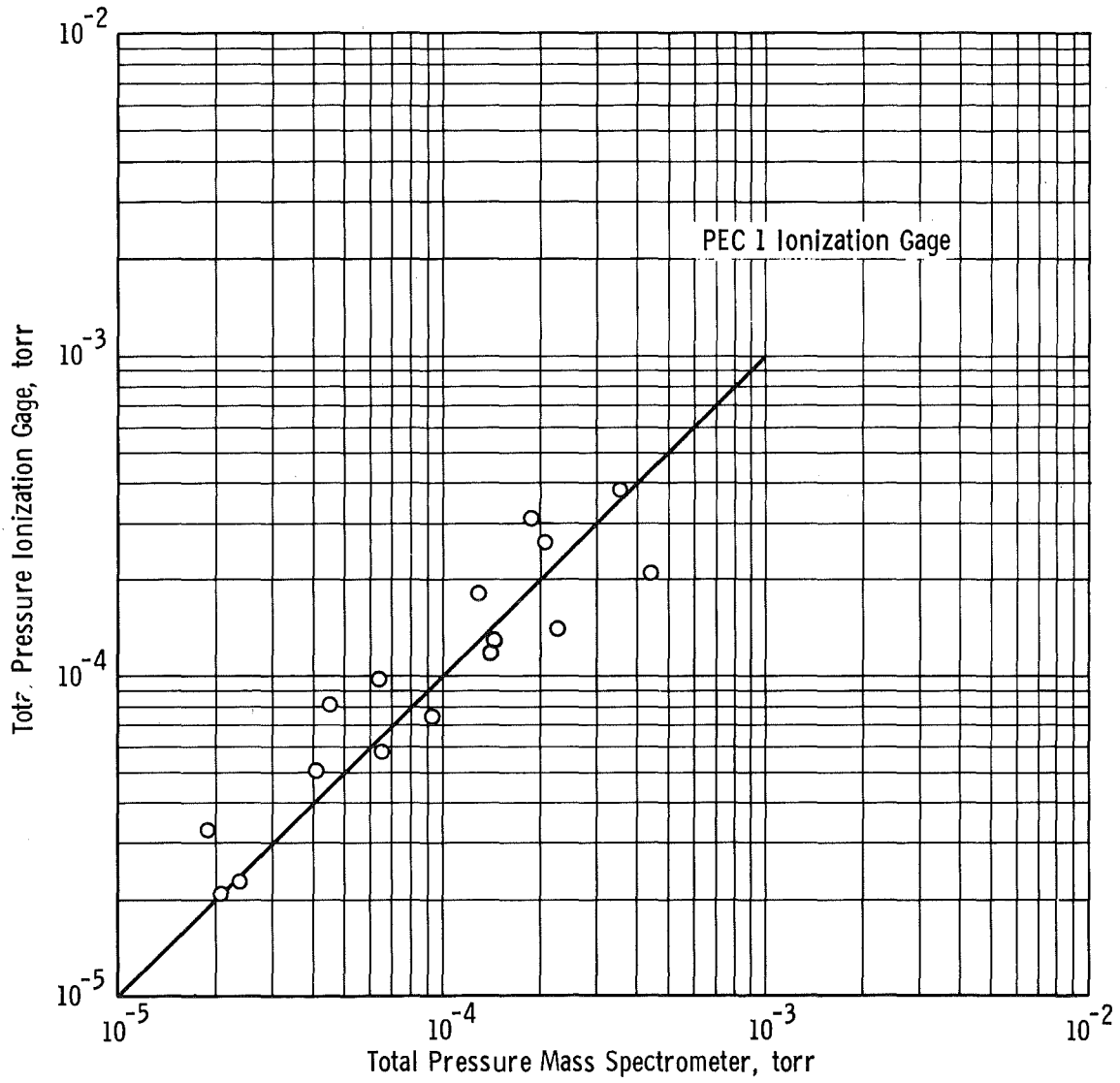


Fig. 2 Ionization Gage Pressure versus Total Mass Spectrometer Pressure

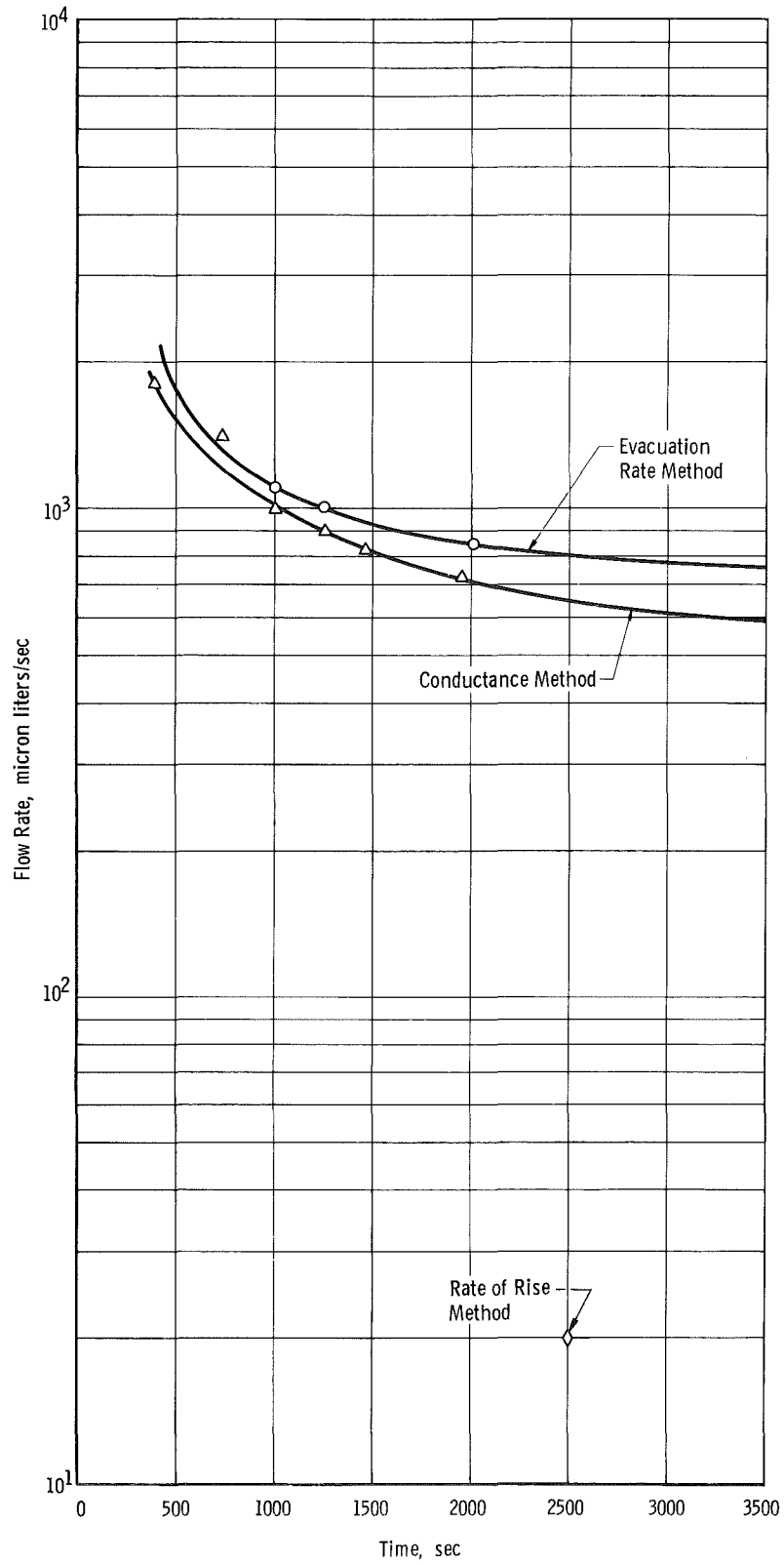


Fig. 3 Comparison of Methods of Outgassing Rate Measurements