

MEMO61588.tex

TO: LIGO engineering

FROM: R. Weiss

CONCERNING: Pressure changes in the beam tubes with temperature and some theory of outgassing.

The question addressed in this memo is the change in the density and constituents of the residual gas in the LIGO beam tubes with temperature. The pressure changes will also occur in the instrumentation chambers since they cannot be effectively isolated given the large pumping speed of an aperture with the size of the beam tube. The pressure changes and the resultant sensitivity change of the gravitational wave interferometers will set a constraint on the temperature stability requirements for the tubes. The processes considered are time average outgassing of the tube walls. The difficult question of the fast variation of the pressure, the so called bursts, is not addressed; although should gas bursts really be a problem their rate and possibly their amplitude will also be temperature dependent.

A second part of the memo discusses some of the theory of the outgassing and possible techniques to make measurements on the vacuum test facility that will improve our knowledge of the outgassing of water.

The fundamental assumption being made in these calculations is that an absolute bakeout of the tubes will never be carried out, but rather, as Boude Moore has suggested, no bakeout or a partial low temperature bakeout will be done should this prove necessary.

### SUMMARY

- 1). Hydrogen pressure from diffusion of dissolved hydrogen in the stainless tubing doubles with every 15 K increase in temperature.
- 2). Hydrogen pressure due to permeation through welds doubles with every 6K increase in temperature.
- 3). Corrosion at welds especially in thin sections is a long term concern and one reason to protect the beam tubes.
- 4). Residual gas water pressure due to surface desorption doubles with every 6 K increase in temperature. The amount of water outgassing is uncertain but is expected to be a major constituent in the LIGO without a bakeout.
- 5). A theory for a  $1/t$  dependence for the water outgassing is developed and compared with data from the 1.5 meter and 5 meter systems as well as with empirical relations found in the literature.
- 6). Some experiments that could be performed on the vacuum test facility are analysed. The most useful measurements for the LIGO are those that determine the number of high activation energy adsorption sites and their occupation probability.

## HYDROGEN

Three processes will be considered: 1) the diffusion and desorption of hydrogen dissolved in the stainless steel, 2) the permeation of hydrogen through the steel, the hydrogen being derived from the atmosphere or by the dissociation of water at locations of corrosion, 3) the permeation through welds.

### 1) Diffusion and release of dissolved hydrogen

The hydrogen outgassing rate is limited entirely by the diffusion of *atomic* hydrogen from the interior of the metal to the surface where, after surface migration, *molecular* hydrogen is formed by recombination. The processes on the surface are complicated. The binding energy of the hydrogen atom to the surface is large,  $\approx 3 \times 10^4$  K \*, so that atomic hydrogen remains bound to the surface at 300 K. The binding of molecular hydrogen can be modelled by a double well potential at the surface, the well closest to the surface (chemisorption) has a depth  $\approx 1.5 \times 10^4$  K while the well furthest from the surface (physisorption) has a depth of  $\approx 6 \times 10^3$  K. The two wells are separated by a potential hill that must be several thousand degrees high (I cannot find measurements of this in the literature, and it may be useful to ask people who have a fast neutral beam machine to measure it). The average time a molecule spends in a well is given by

$$\tau = \tau_0 e^{T_b/T}.$$

$\tau_0 = 10^{-13}$  seconds, a typical lattice oscillation period,  $T_b$  is the binding energy in K, and  $T$  is the operating temperature usually 300 K. The dwell time in the outer well is  $\approx 10^{-5}$  seconds, while it is  $\approx 10^{30}$  seconds in the inner well at 300K. The molecular hydrogen escapes from the inner well only because of the energy released in recombination of the atoms which is  $5 \times 10^4$  K. Once the molecular hydrogen has been released from the surface and thermalized by further collisions with the walls, it has a small probability of returning to the inner well because of the potential hill.

The diffusion of atomic hydrogen out of the metal is governed by thermally activated stochastic motion where the mean free path and activation energy for the motion are incorporated in the diffusion constant  $D(T)$  given in  $\text{cm}^2/\text{sec}$ . The flux of atoms arriving at the surface,  $J$  atoms/ $\text{cm}^2$  sec, is related to the density of hydrogen atoms in the metal,  $\rho_H$ , by

$$J_H = \rho_H \left( \frac{D(T)}{\pi t} \right)^{1/2}$$

where  $t$  is the time in seconds. The diffusion constant as a function of temperature is

$$D(T) = 3.3 \times 10^{-2} e^{-T_{act}/T}$$

where  $T_{act} = 8.1 \times 10^3$  K. The relation for the flux assumes that the density,  $\rho_H$ , deep inside the metal remains constant otherwise the flux will drop exponentially with time (the

---

\* Energy will be given in terms of temperature,  $E = k_b T$  where  $k_b$  is Boltzmann's constant.

onset of the exponential behaviour begins  $t \sim \frac{\pi l^2}{16D(T)}$ , approximately  $2 \times 10^4$  years in a 3/16 inch thick piece of stainless at 300K)

The fractional change in the outgassing flux with change in temperature,  $\Delta T$ , is

$$\frac{\Delta J}{J} = \frac{T_{act} \Delta T}{2T^2}.$$

At 300K the hydrogen outgassing rate doubles for every 15K temperature increase.

The density,  $\rho_{H_2}$ , of molecular hydrogen in the beam tubes depends on the ratio of the tube area,  $A$ , to the total pumping speed,  $F$ , and depends as well on the initial density of atomic hydrogen dissolved in the stainless steel as

$$\rho_{H_2}(T, t) = \frac{J_H(T, t)A}{2F} = \rho_H(0) \left( \frac{D(\infty)}{\pi t} \right)^{1/2} e^{-\frac{T_{act}}{2T}} \frac{A}{2F}$$

Boude Moore believes that he can get stainless steel with an equivalent mass ratio of  $H_2$  to host steel of 1 part per million, this corresponds to  $\rho_H(0) = 5 \times 10^{18}$  atoms/cm<sup>3</sup>. The ratio of surface area ( 2 km tube length, 48 inches diameter) to pumping speed (18000 liters/sec) being planned is 4.25 sec/cm. The  $H_2$  density and pressure in the tube as a function of time and temperature are

$$\rho_{H_2} = \frac{1.9 \times 10^{14}}{(t(yr))^{1/2}} e^{-4050/T} \text{ molecules/cc} \implies \frac{6.5 \times 10^{-3}}{(t(yr))^{1/2}} e^{-4050/T} \text{ torr}$$

The hydrogen pressure at 300 K after 1 year is then expected to be

$$P_{H_2} = 9 \times 10^{-9} \text{ torr}$$

and a 15K increase in temperature would raise the pressure to  $1.8 \times 10^{-8}$  torr.

## 2) Permeation of hydrogen through tubes and bellows

Permeation is the process of solution of hydrogen incident on the outer surface of the tube followed by diffusion through the tube and desorption on the inner surface. The hydrogen incident on the outside comes from atmospheric  $H_2$ , which has an atmospheric abundance of  $4 \times 10^{-4}$  torr ( $1.2 \times 10^{13}$  molecules/cc), and from the dissociation of water at points of corrosion. The density of atomic hydrogen dissolved in the iron is proportional to the square root of the outside pressure of molecular hydrogen (detailed balance at equilibrium, the reaction is  $H_2 = 2H$ ) with the proportionality constant being the solubility. The density,  $\rho_H$ , of dissolved hydrogen atoms/cc is given in terms of the external molecular hydrogen density,  $\rho_{H_2}$ , by

$$\rho_H = s(T) \rho_{H_2}^{1/2}$$

where  $s(T)$  is the temperature dependent solubility in units of cm<sup>-3/2</sup> given by

$$s(T) = s_0 e^{-T_{sol}/T}.$$

The activation temperature for solution  $T_{sol} = 3400$  K and  $s_0 \approx 2 \times 10^9$  cm<sup>-3/2</sup>. The dissolved hydrogen density in equilibrium with atmospheric hydrogen at 300 K is  $1 \times 10^{11}$  atoms/cc and that in equilibrium with water at 100% humidity ( $\rho_{H_2O} = 1 \times 10^{18}$  molecules/cc) is  $3 \times 10^{13}$  atoms/cc. Both quantities are much smaller than the initial hydrogen density in the stainless steel and will not be considered further, but it is worth noting that permeation sets a lower limit on the outgassing should one decide to build the LIGO out of thin wall tubing or bellows.

### 3) Permeation through welds

Permeation through welds can be different than through the stainless steel since the welded material may be closer to having the properties of ordinary steel than stainless. The following estimates assume that the welds behave as ordinary iron which is a pessimistic but not unreasonable assumption. The solubility and diffusion of hydrogen in ordinary iron is substantially larger than in stainless and furthermore the welds are more likely to be locations of corrosion than the parent metal of the tubes.

The fraction of the area covered by welds is estimated as

$$\frac{A_{weld}}{A_{tube}} = \frac{wp}{2\pi a} + \frac{w}{L_{sec}}$$

where  $w$  is the width of the weld, say 1/4 inch,  $a$  the radius of the tube, 24 inches,  $p$  the pitch of the spiral welds on the tube, 3, and  $L_{sec}$  is the length of a single section of tube before welding, 40 feet. The first term comes from the spiral welds and the second from the circumferential welds at tube joins. The area ratio is  $\approx 6 \times 10^{-3}$ .

The diffusion constant of atomic hydrogen through ordinary iron is much larger than for stainless steel and given by

$$D(T) = 2.4e^{-6310/T}$$

The solubility at corrosion points is  $10^3$  to  $10^4$  times higher than in the stainless steel. This qualitative information comes from *Vacuum Engineering* Holkeboer, Jones, Pagano, and Santeler, Boston Technical Publishers, 1967. If one assumes that  $s_0$  changes by a factor of  $10^4$  but the activation energy for solution remains the same, the flux of molecular hydrogen permeating into the system through the welds from the dissociation of atmospheric water could be as large as

$$J_{H_2} = \frac{D(T)s(T)\rho_{H_2O}^{1/2}}{2h} = \frac{3 \times 10^{22}e^{-9710/T}}{h}$$

$h$  is the thickness of the weld in cm. Most of the weld area is on tubes,  $h = 3/16$  inch, about 5% of the weld area is on bellows,  $h = .030$  inches. Combining the previous factors leads to an estimate of the permeation through the welds on the tubes at 300K that could contribute

$$P_{H_2}(\text{welds on tubes}) \leq 8 \times 10^{-10} \text{ torr}$$

to the hydrogen pressure and double with each 6 K increase in temperature, but with a diffusion time constant of about 9 months. The permeation through the welds on bellows could contribute

$$P_{H_2}(\text{welds on bellows}) \leq 3 \times 10^{-10} \text{ torr}$$

and double with each 6 K increase in temperature with a diffusion time of 7 days.

The permeation sets an upper bound on the pressure, which could become larger with time as the amount of corrosion of the apparatus increases. At the outset of the LIGO it does not appear, however, to be the limiting factor on the pressure. I would recommend that a continuous inventory be kept of the number of welds on the system as the design evolves and this question be revisited periodically throughout the design phase of the LIGO. The corrosion should also be considered as a factor in the decision on whether to protect the tubes with a cover.

## WATER

General experience with the outgassing of water in unbaked stainless steel systems has been characterized by Dayton, B.B. *Transactions of the Eighth Vacuum Symposium*, Pergamon p 42 1962, as

$$J_{H_2O}(300K) \simeq \frac{1.7 \times 10^{-7}}{t(hr)} \text{ torr liters/sec cm}^2 \implies \frac{5 \times 10^{12}}{t(hr)} \text{ molecules/sec cm}^2.$$

after a few hours of pumping.

Edwards (*J. Vac Sci Technol.*, vol 14, p 606, 1977) also gives an empirical relation for a stainless steel system once baked but refilled for an hour with room air (assume 50% humidity at 300K, 10 torr of  $H_2O$ ). He finds

$$J_{H_2O}(300K) \simeq \frac{3.3 \times 10^{-9}}{t(hr)} \text{ torr liters/sec cm}^2 \implies \frac{9.9 \times 10^{10}}{t(hr)} \text{ molecules/sec cm}^2.$$

after a few hours of pumping and extending to times of 300 hours. There are several difficulties with these empirical relations. The first, as Boude Moore has pointed out, is that the integral for the total gas desorbed with time diverges, so that at some time the outgassing rate must decrease more quickly with time. The second, more important for this memo, is that they do not allow an estimate of the temperature dependence. Bad as the relations may be, Dayton's is not far from predicting the upper limit derived from the measurements of water outgassing in the 1.5 meter prototype after 4 years of accumulated pumping. This system was never baked.

In order to make the needed estimates, the physics at the surface has to be modelled. The model will be guided by the  $1/t$  dependence and our experience in pumping and filling unbaked systems but cannot be completely specified since the surface physics is really unknown. The concept is to assume that the surface can be described by a distribution function of water adsorption sites which are associated with different activation energies. This assumption alone will give the  $1/t$  dependence over a range of times and seems quite

reasonable since no surface is microscopically uniform. The specific distribution of the sites is established by surface treatment ( cleaning methods, surface porosity,.. ) and will be the major unknown in the model. I believe enough model independent information can be derived from bulk measurements so that, the prior and planned tests have some predictive value.

Assume that before pumping the surface is saturated, each adsorption site is occupied. The surface density of adsorbed water molecules in a small band of activation energies,  $\delta T_{act}$  around  $T_{act}$  is given as

$$\delta\sigma = n\sigma_0\theta(T_{act})\delta T_{act}.$$

$\sigma_0 \simeq 3 \times 10^{15}$  molecules/cm<sup>2</sup> is the saturation surface density associated with a single monolayer of water. (The density includes a factor of 3 to allow for the real surface which has roughness on micron scales.)  $n$  is the number of monolayers that can be bound to the metal, usually  $n$  is 1 but the surface is really three dimensional with pores and microcracks on Angstrom scales which offer more binding sites below the "surface". Although a new unpumped surface may have many monolayers of water adsorbed on it, the only surface that matters in the outgassing is the one closest to the surface. The desorption activation energy for water on water is only 5500 K, considerably lower than the water to the metal, so that these water layers pump out rapidly. The coverage distribution function,  $\theta(T_{act})$ , (the fraction of the total sites having an activation energy  $T_{act}$ ) is normalized as

$$\int_0^\infty \theta(T_{act})\delta T_{act} = 1.$$

If the system has been pumping since time  $t$ , at a sufficient pumping speed so that readsorption on the surface is unimportant, the differential flux of molecules leaving the surface from sites characterized by an activation energy  $T_{act}$  in the range  $\delta T_{act}$  is

$$dJ_{out}(t) = \left( \frac{n\sigma_0\theta(T_{act})P(T_{act}, t)}{\tau(T_{act})} \right) \delta T_{act}. \quad \text{eq (1)}$$

$\tau(T_{act})$  is the residence time of the molecule on the surface at a site with activation energy  $T_{act}$  given by

$$\tau(T_{act}) = \tau_0 e^{T_{act}/T}.$$

Assuming no readsorption, the probability that a site with activation energy  $T_{act}$ , originally filled, is still occupied after a time  $t$  of continuous pumping is

$$P(t) = e^{-\frac{t}{\tau(T_{act})}}$$

The outgassing as a function of time is the integral of eq (1) over the distribution function

$$J_{H_2O}(t) = \frac{n\sigma_0}{\tau_0} \int_0^\infty \theta(T_{act}) e^{-\frac{T_{act}}{T}} e^{-\frac{t e^{-\frac{T_{act}}{T}}}{\tau_0}} \delta T_{act} \quad \text{eq (2)}$$

Since we do not know the physics at the surface, the best thing to do is to choose a distribution function that is easy to manipulate and is not unreasonable. One possibility is a function which is uniform in activation energy upto a maximum  $T_m$ ,

$$\theta(T_{act}) = \frac{1}{T_m} \quad 0 \leq T_{act} \leq T_m$$

$$\theta(T_{act}) = 0 \quad T_{act} > T_m$$

The outgassing rate for this distribution in the limit when  $T_m \gg T$  is given by

$$J_{H_2O}(t) = \frac{n\sigma_0 T}{T_m t} e^{-\frac{T}{T_m}}.$$

The outgassing rate varies as  $1/t$  until the most tightly bound sites begin to desorb.

A seemingly more realistic distribution function would have more loosely bound sites than tightly bound ones such as an exponential distribution in activation energy with an average energy  $T_0$ , given by

$$\theta(T_{act}) = \frac{1}{T_0} e^{-\frac{T_{act}}{T_0}}$$

The outgassing rate for this distribution when  $\frac{T}{T_0} \ll 1$  is approximately

$$J_{H_2O}(t) = \frac{n\sigma_0 T}{T_0 t} \gamma \left( 1 + T/T_0, \frac{t}{\tau_0} \right).$$

As  $t/\tau_0$  becomes much larger than 1, the incomplete gamma function becomes 1. The exponential distribution function and the uniform one give similar outgassing functions at times smaller than  $\tau(T_m)$ . The total gas stored on the surface and the average residence time diverges for the exponential distribution, so that in subsequent estimation I will use the uniform distribution.

The bounds that can be set on the temperature dependence of the pressure come from our experience with the 1.5 meter system and the pumping of the 5 meter system. I will relate these experiences to the Dayton and Edwards formulae. The problem is separating  $n$  from  $T_m$

From the 1.5 meter system

The most constraining data comes from the measurement of the water remaining in the 1.5 meter system which has been held by ion pumps at a pressure below  $3 \times 10^{-7}$  torr for an accumulated time of 4 years. The volume of the system is 200 liters, the geometric surface area is  $4 \times 10^4$  cm<sup>2</sup> and the pumping speed of the pumps for water began at 60 liters/sec and is now at 15 liter/sec. The final value of the ratio of area to pumping speed is 2.7 sec/cm, about 1/2 of the value being projected for the LIGO. The present outgassing rate is

$$J_{H_2O}(4yr) \leq 3 \times 10^{-12} \text{ torr liters/sec cm}^2 \implies 9 \times 10^7 \text{ molecules/sec cm}^2$$

The maximum residence time for water would have to be 4 years at 300K so that in the uniform model  $T_m$  would be  $1.46 \times 10^4$  K or larger. The value of the outgassing rate gives  $n = 180$ . For the same value of  $T_m$  the Dayton relation gives  $n = 290$ , while the Edwards relation gives 5.7.

From the 5 meter system

The initial pump down of the individual tanks of the 5 meter system gives the following information. The volume of a tank  $2.6 \times 10^3$  liters, the surface area  $1.1 \times 10^5$  cm<sup>2</sup> and the pumping speed at the tank is 1000 liters/sec. The ratio of surface area to pumping speed is .11 sec/cm. The outgassing rates measured were

$$J_{H_2O}(3hr) = 1.5 \times 10^{-9} \text{ torr liters/sec cm}^2 \implies 4.5 \times 10^{10} \text{ molecules/sec cm}^2$$

$$J_{H_2O}(10hr) = 5 \times 10^{-10} \text{ torr liters/sec cm}^2 \implies 1.5 \times 10^{10} \text{ molecules/sec cm}^2$$

Using  $T_m = 1.46 \times 10^4$  K gives  $n = 8.8$ .

Values for the activation energy in the literature range from  $7 \times 10^3$  K from surface sites to  $1.5 \times 10^4$  K for diffusion out of pores in the surface.

The temperature rise required to double the outgassing rate after a long pumpout is determined by  $T_m$  and the approximation that  $\tau(T_m) \approx t$ .

$$\Delta T(\text{double}) = \frac{T^2}{T_m}$$

For  $T_m = 1.46 \times 10^4$  K, the water outgassing and pressure doubles every 6K at 300 K.

The pressure of water is much more uncertain since the initial surface loading is dependent on surface condition and cleaning.  $n$  can lie between 300 to 5. Using the uniform model and  $T_m = 1.46 \times 10^4$  K, the water pressure in the LIGO is

$$\rho_{H_2O} = \frac{AJ_{H_2O}(t)}{F} \approx \frac{n2.8 \times 10^{-10}}{t(\text{yr})} \text{ torr}$$

Using  $n = 300$  the water pressure after 1 year would be  $8.4 \times 10^{-8}$  torr and would go to  $1.7 \times 10^{-7}$  with a temperature increase of 6 K.

## SOME OUTGASSING THEORY AND SUGGESTIONS FOR MEASUREMENTS

The key variable to know in order to predict the long term water outgassing in the LIGO is the number of adsorption sites with high activation energy. The number of these sites must depend on the surface treatment while the probability of initial occupation most likely depends on the cleaning chemistry. The value of  $n$ , though useful for initial pumpdown predictions, is less important.

What can be learned concerning the free parameters in the outgassing function from better direct gas flow and accumulation rate measurements?



The vacuum system dynamics satisfies the conservation of molecules.

$$dN/dt(\text{desorbed}) = dN/dt(\text{readsorbed}) + dN/dt(\text{gas in volume}) + dN/dt(\text{pumped out}). \quad \text{eq (3)}$$

The desorption rate is given by equations 1 and 2. The differential readsorption rate is given by

$$dJ_{in}(t) = \left( \frac{\rho v_{th}}{4} \right) f_0 \theta(T_{act}) (1 - P(T_{act}, t)) \delta T_{act} \text{ molecules/sec cm}^2. \quad \text{eq (4)}$$

$\rho$  is the residual water gas particle density,  $v_{th}$  is the thermal velocity of the water and  $f_0$  is the probability of sticking independent of the site activation energy. The readsorption rate assumes that there is maximum one molecule per site and that the probability of site occupancy does not depend on whether a neighboring site is full or empty.

#### Equilibrium determination of $\theta(T_{act})$

Equilibrium is attained when the system is sealed, no gas being pumped out, and the pressure in the volume has become constant. The desorption and readsorption rates then become equal. Detailed balance requires that this be so for each element of the distribution function  $\theta(T_{act})$ . The probability of site occupancy as  $t \rightarrow \infty$  becomes

$$P(T_{act}, t \rightarrow \infty) = \frac{b}{1 + b}$$

where

$$b = \frac{\rho v_{th} f_0 \tau(T_{act})}{4n\sigma_0}.$$

A sensitive method to determine the distribution function (especially the number of high activation energy sites of relevance to the LIGO) is to measure the equilibrium pressure of a sealed system with temperature. This is best carried out in a regime where  $b \ll 1$  by adjusting the total number of molecules introduced into a baked system. It is useful to operate at temperatures where the residence time, at the highest activation energy sites, is short enough so that one can live with the experiment. Figure 1 shows the pressure for  $b = 1/2$  and the residence time as a function of activation energy for a system at 300K. If the highest activation energy is  $1.5 \times 10^4$  K, the temperature has to be raised to 500 K in order to reduce the residence time, and therefore also the equilibration time, to 1 second.

The experiment is straightforward. Pump the system while being baked. By keeping track of the integrated outflow of  $H_2O$  with the RGA, one gets a poor estimate of  $n$ . Stop pumping when the pressure of water is low enough so that  $b$  for the highest activation temperature is sufficiently below 1, say between .1 to .01. Now, with the apparatus still hot introduce a known amount of water and measure the equilibrium pressure as a function of a slow cool down. Figure 2 shows the calculated results of such an experiment using a uniform distribution for various values of  $T_m$ , the curves are extremely sensitive to the value of  $T_m$ .

#### The theory of the experiment

The number of water molecules are accounted for by

$$N(in) = N(gas) + N(surface).$$

The number of water molecules in the gas is

$$N(gas) = \rho V$$

The number on the surface is

$$N(surface) = An\sigma_0 \int_0^{\infty} \theta(T_{act})P(T_{act})\delta T_{act}.$$

At equilibrium, if  $b \ll 1$ ,

$$P(T_{act}) = \frac{f_0 v_{th} \tau(T_{act}) \rho}{4\sigma_0 n}$$

The equilibrium gas density is

$$\rho = \frac{\rho_0}{1 + \left( \frac{A f_0 v_{th}}{4V} \right) \langle \tau(T_{act}) \rangle}.$$

$\rho_0 = N(in)/V$ , the gas density with no adsorption on the walls, and  $\langle \tau(T_{act}) \rangle$  is the residence time weighted over the distribution function given by

$$\langle \tau(T_{act}) \rangle = \int_0^{\infty} \theta(T_{act}) \tau(T_{act}) \delta T_{act}.$$

For the uniform distribution

$$\langle \tau(T_{act}) \rangle = \left( \frac{T}{T_m} \right) \tau(T_m). \quad \frac{T}{T_m} \gg 1$$

Accumulation rate determination of  $\theta(T_{act})$

Another method, not as good as the equilibrium technique, is to measure the accumulation rate of water in a system sealed after a time  $t_0$  of pumping. The measurement is an application of eq (3) with  $dN/dt(\text{pumped out}) = 0$  applied shortly after  $t_0$ . The desorption rate is

$$dN/dt(t_0) = AJ_{out}(t_0).$$

The accumulation rate is

$$dN/dt(t_0) = \frac{d\rho}{dt}(t_0)V$$

where  $V$  is the volume of the system. The molecular gas density in the system at  $t_0$  is

$$\rho(t_0) = \frac{AJ_{out}(t_0)}{F}$$

where  $F$  is the pumping speed before sealing. The readsorption rate is given by the integral of eq (4) over the activation temperatures

$$dN/dt(t_0) = \left( \frac{Av_{th}f_0}{4F} \right) \left( 1 - \int_0^\infty \theta(T_{act}) e^{\frac{-t_0}{\tau(T_{act})}} \delta T_{act} \right).$$

Solving the equation for the accumulation rate gives the result

$$\frac{d\rho}{dt}(t_0+) = \left( \frac{AJ_{out}(t_0)}{V} \right) \left( 1 - \left( \frac{Av_{th}f_0}{4F} \right) \left( 1 - \int_0^\infty \theta(T_{act}) e^{\frac{-t_0}{\tau(T_{act})}} \delta T_{act} \right) \right).$$

The first term in brackets on the right is just the accumulation rate if there is no readsorption.

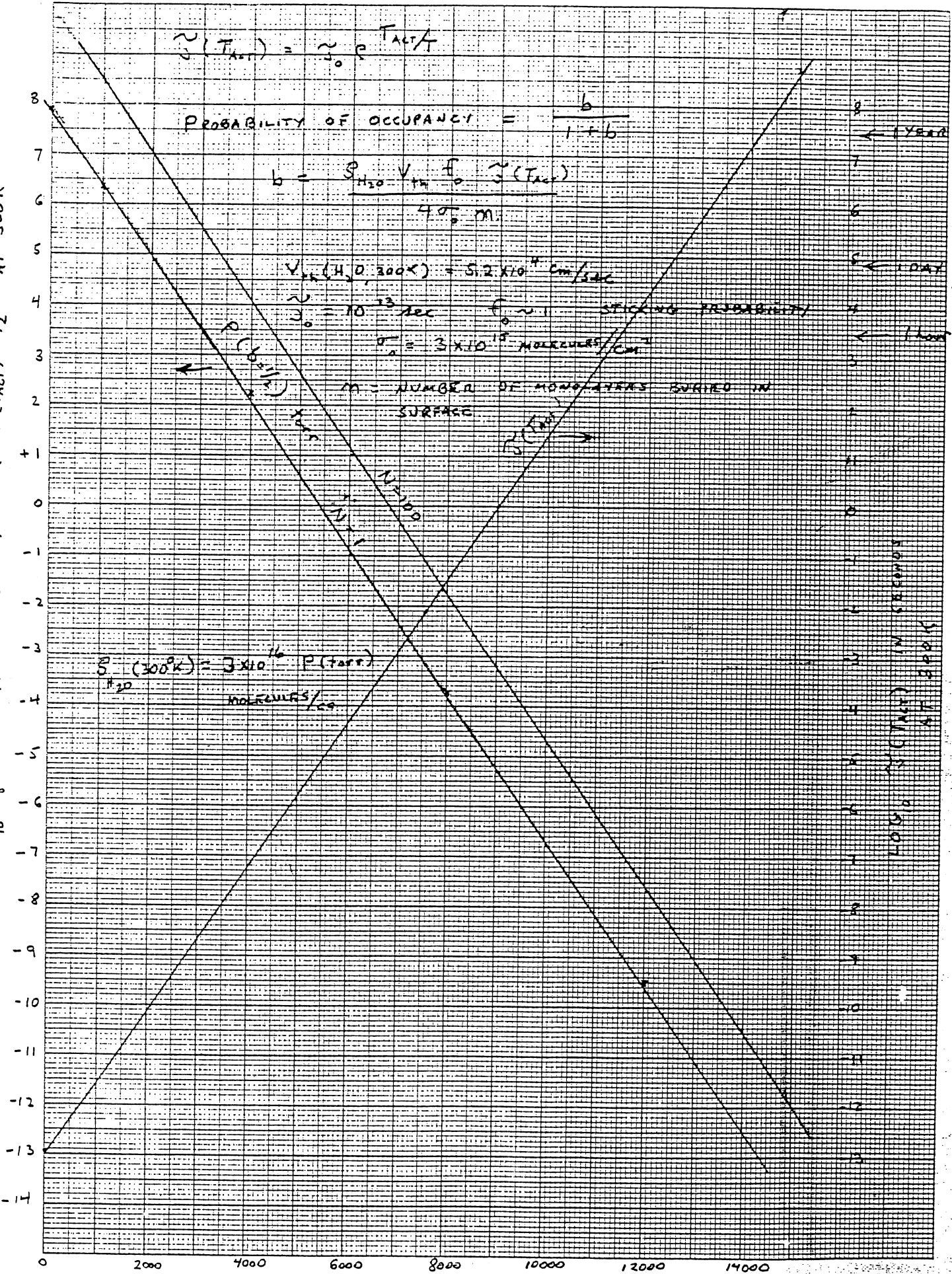
For the uniform distribution the accumulation rate becomes

$$\frac{d\rho}{dt}(t_0+) = \left( \frac{AJ_{out}(t_0)}{V} \right) \left( 1 - \left( \frac{Av_{th}f_0}{4F} \right) \left( 1 - \frac{T}{T_m} \int_{\frac{t_0}{\tau(T_m)}}^\infty \frac{e^{-y}}{y} \delta y \right) \right).$$

The integral is shown in figure 3. At small values of  $\frac{t_0}{\tau(T_m)} = z$  it varies  $\approx |\ln(z)|$  while at large values it varies as  $\frac{e^{-z}}{z}$ .

The major difficulty with the accumulation technique as a means of determining the number of high energy activation sites is that it is only logarithmically sensitive to the high activation energy sites at room temperature unless one waits a long time or runs the system at elevated temperatures.

LOG<sub>10</sub> EQUILIBRIUM PRESSURE (TORR) FOR P(TACT) = 1/2 AT 300K



(FIGURE 1)

T<sub>ACT</sub> °K

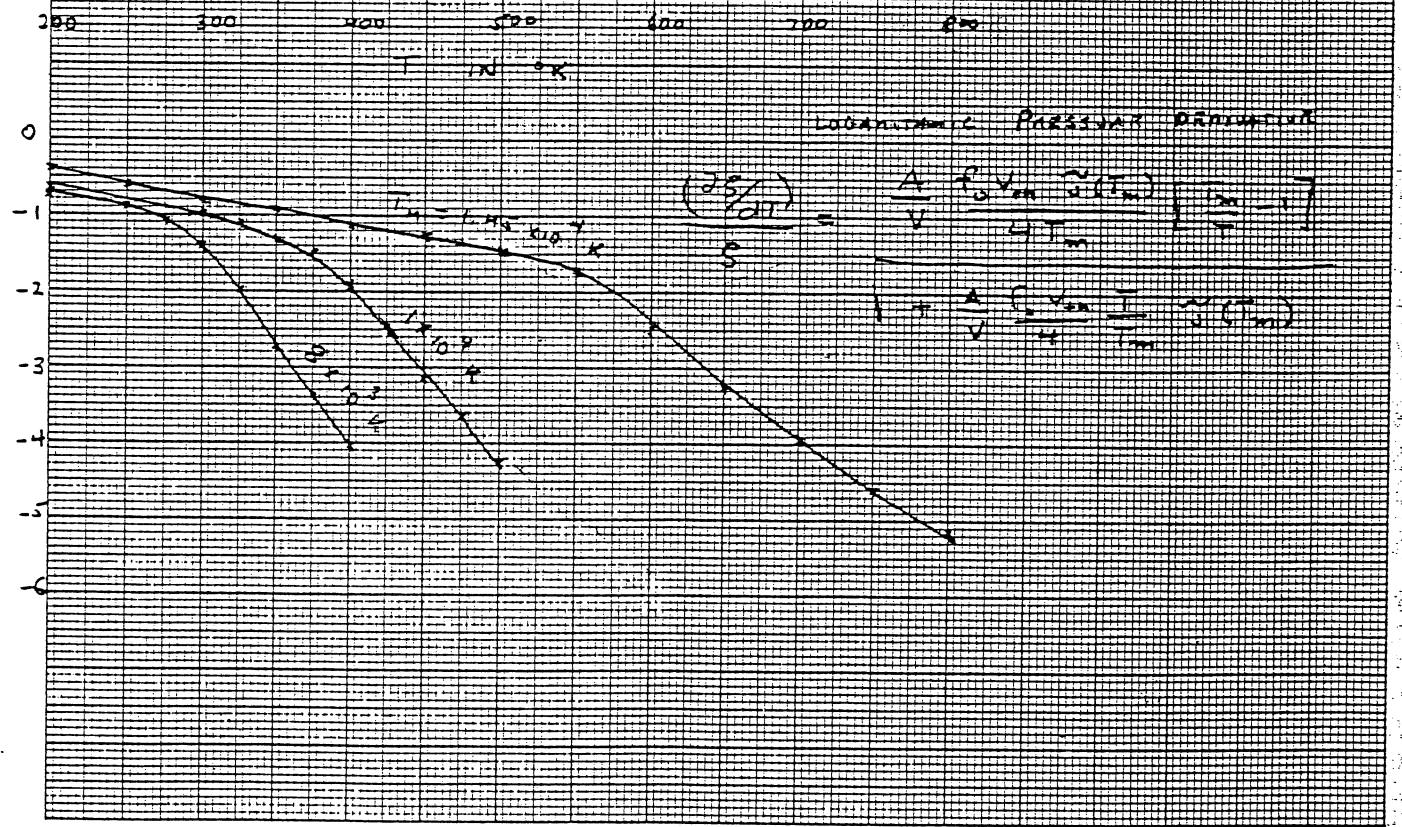
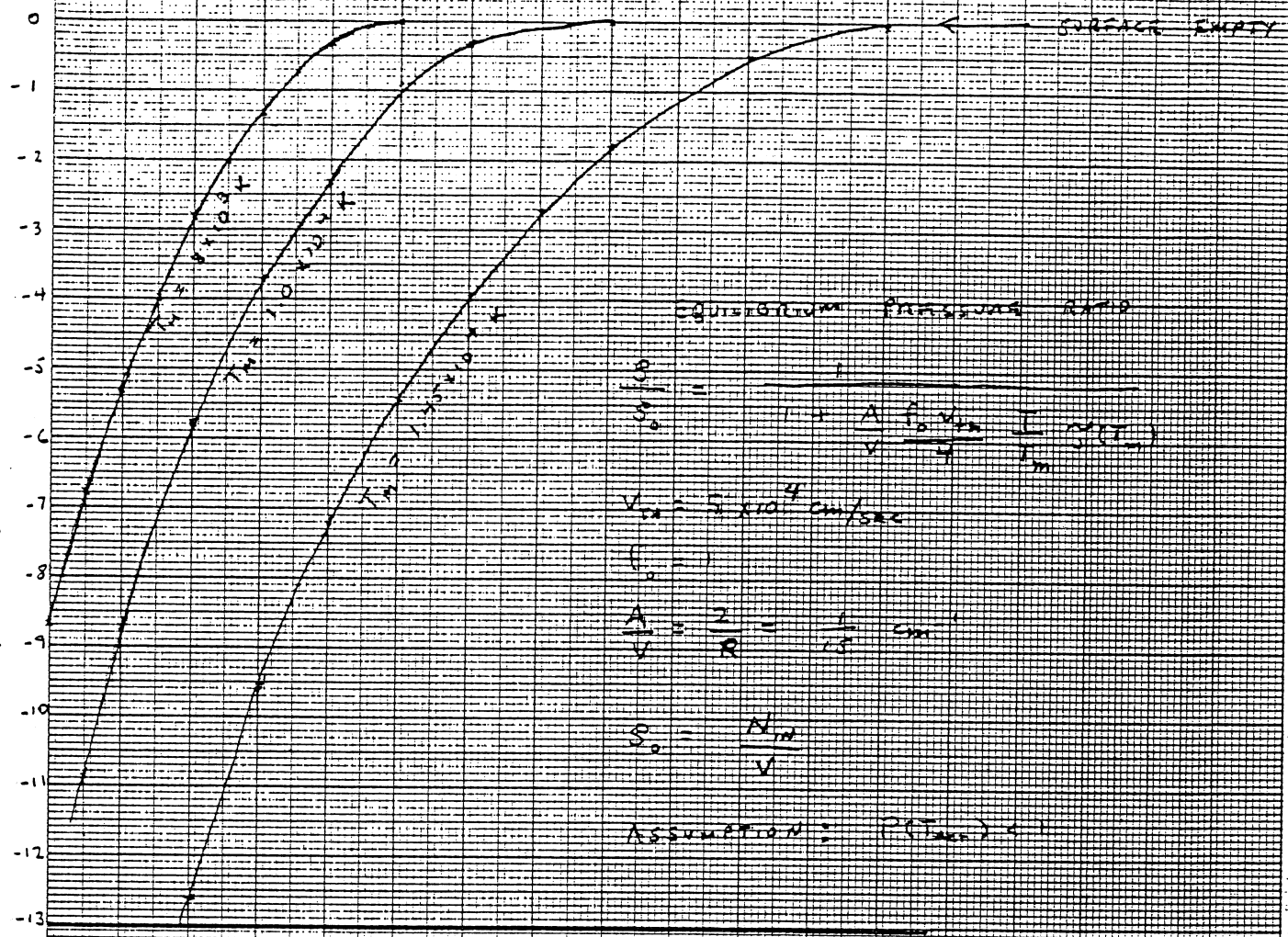
USING UNIFORM DISTRIBUTION OF  $\Theta(T_{act})$

SQUARE 10 X 10 TO THE CENTERLINE AS 8014-60

© General Electric Company, 1954. GEORGIA INSTITUTE OF TECHNOLOGY, Atlanta, Georgia, U.S.A.

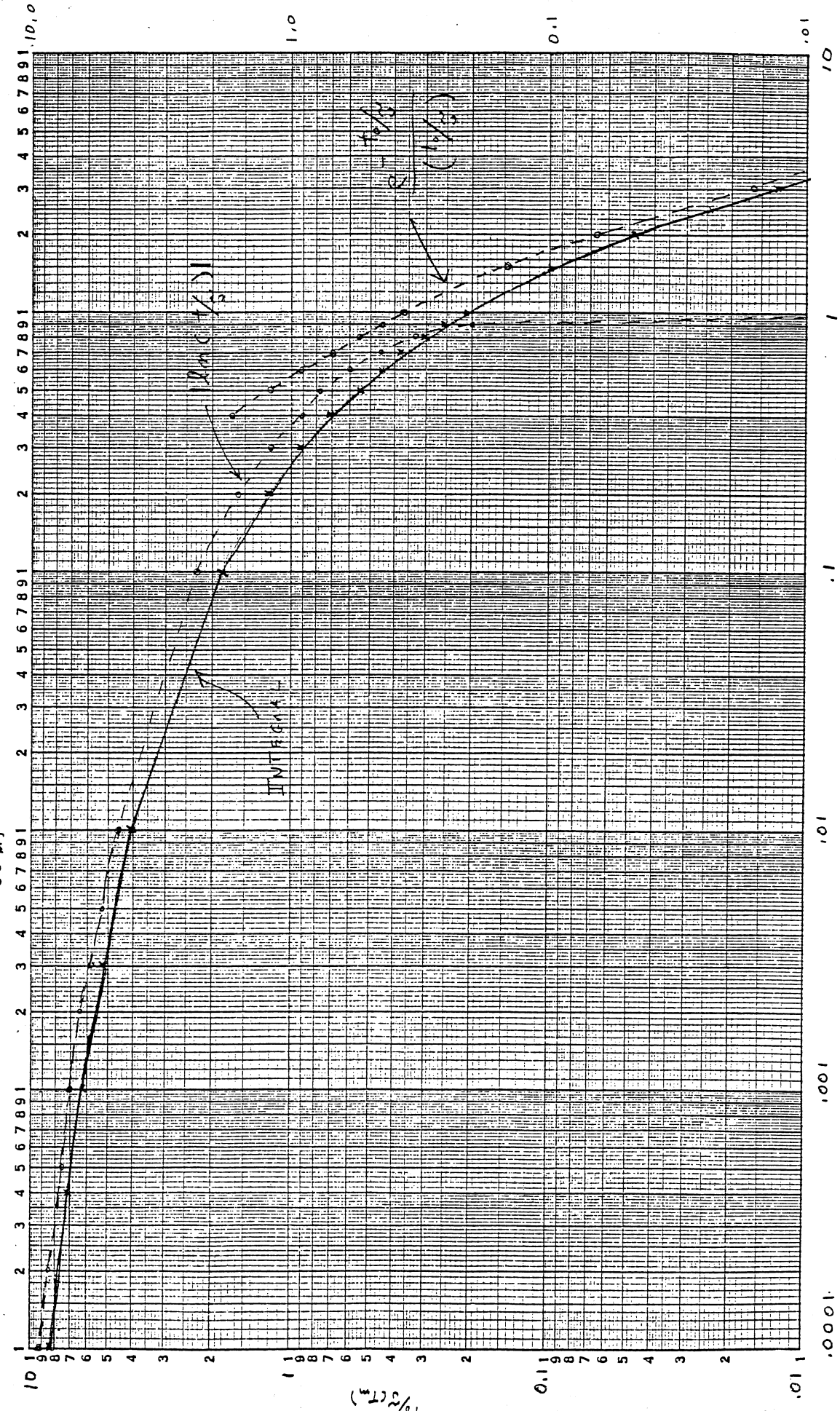
LOG<sub>10</sub> S/S<sub>0</sub>

LOG<sub>10</sub> (dS/dT)/S



(FIGURE 2)

$\int_0^{\infty} \frac{e^{-y}}{y} dy$   
 $t_0/\sqrt{3}(T_M)$   
 FRACTIONAL COVERAGE INTEGRAL  
 FOR UNIFORM DISTRIBUTION



$t_0/\sqrt{3}(T_M)$

(FIGURE 3)