EXPERIMENTAL DETERMINATION OF ACCOMMODATION COEFFICIENTS AS FUNCTIONS OF TEMPERATURE FOR SEVERAL METALS AND GASES

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ABSTRACT

The accommodation coefficients for the gases and metals tested vary rapidly in the range where the gas temperature is within approximately 50°C. of the filament temperature.

When the temperature excess becomes large, the α of argon, nitrogen and helium on platinum is approximately .7, .5 and .2, respectively, and on tungsten approximately .5, .35 and .15, although the actual value depends upon both filament and gas temperature.

Variation in pressure up to 150 microns was found to have a negligible effect on α.

All gases and metals tested gave smooth curves of α versus temperature except helium on tungsten at a gas temperature of 80° K., which exhibited a sharp discontinuity at a filament temperature of approximately 225° K. and a pressure of 34 microns.

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INTRODUCTION

The interaction phenomenon between gas and surface molecules becomes of increasing importance because of the widespread work with hot wires at low pressures that is being done at present.

It is the purpose of this paper to present data which may aid in the formulation of a physical theory to explain this phenomenon more satisfactorily.

Some work on a quantum mechanical theory of collisions of gas atoms with solids was done by Devonshire (1), who assumed the potential energy between the molecules is given by a Morse function and showed that the values of the constants could be deduced from the shape of the accommodation coefficient versus temperature curve.

Of more immediate interest, however, in the field of jet propulsion is the calculation of heats of dissociation of gases. If the total heat loss from the filament is measured as the filament temperature is increased, the trend of α with temperature may be calculated. Then as the filament heats to a temperature at which dissociation of the gas occurs significantly, the ΔH measured will increase sharply to a value far greater than what would be expected from the change of α with temperature alone. Since α has been shown to be independent of pressure in the "free molecule" range, then by changing the pressure at a given filament temperature the change in energy supplied to the gas may be determined as a function of pressure. This relation is linear if no dissociation occurs, but is not linear for a gas undergoing dissociation, as the number of moles changes. From this data, heats of dissociation and equilibrium constants may be determined. This method was originally due to Langmuir who determined the heat of dissociation of hydrogen in this manner. (2)

The accommodation coefficient was originally defined by Knudsen as the fractional extent to which molecules which strike a solid surface have their temperature "accommodated" to the temperature of the surface.

Langmuir later redefined it in terms of energy exchange rather than temperature "adjustment". It is this definition which is used in the present work.

Since many of the previous investigations of the accommodation coefficient have been based on Knudsen's definition, the observations were necessarily made using only small temperature differences between gas and surface because it was necessary that the molecules leaving the surface have approximately a "normal" distribution of velocities. As ΔT increases, the departure from the desired distribution becomes larger. As a result of this small

ΔT restriction, the variation of accommodation coefficient with temperature was difficult to obtain because the gas temperature was the only temperature which could be changed arbitrarily. In practice, the method of changing the gas temperature was to immerse the bulb in a constant temperature bath, and suitable baths are rather limited in number.

Using Langmuir's definition of the accommodation coefficient, the ΔT restriction is removed and the variation of α with temperature may be more readily accomplished by holding the bulb temperature constant and varying the filament temperature electrically.

LITERATURE SURVEY

Definition and Determination of the Accommodation Coefficient

The suggestion was made by Poisson, in analogy with phenomena of viscous slip, that at a wall bounding an unequally heated gas there might be a discontinuity of temperature. Smoluchowski verified that the analogy was valid by performing suitable experiments on thermal conductivities at low pressures. The theory developed by Smoluchowsky introduced the effect of accommodation in a way which is somewhat different than what has since come in to general use.

The more generally accepted point of view on the theory of heat conduction at these pressures was developed later by Knudsen involving a consideration of the mechanism of energy transfer by individual molecules incident on the hot surface. Knudsen introduces a constant, called the accommodation coefficient, which

> "can be defined as standing for the fractional extent to which those molecules that fall on the surface and are reflected or re-emitted from it, have their mean energy adjusted or 'accommodated' toward what it would be if the returning molecules were issuing as a stream out of a mass of gas at the temperature of the wall." (3)

The molecules leaving the hot surface have a mean energy corresponding to some temperature lower than the temperature of the surface. If this temperature be denoted by T_r and if the temperature of the surface and of the incident molecules be denoted by T_s and T_i, respectively, the α is defined by the relation

$$\alpha \equiv \frac{T_r - T_i}{T_s - T_i}$$

To determine the value of α experimentally, suppose we have a fine wire in a cylindrical tube maintained at temperature T_s by electric current, in which there is a monatomic gas* at a pressure so low that the mean free path is large compared with the radius of the tube. (4) If the diameter of the wire is very small compared with the tube, then a molecule leaving the wire will collide with the walls of the tube many times before again striking the wire. So, the temperature of the molecules which strike the wire may be considered to be at the tube temperature.

If we assume that there are f(c) dc molecules per c.c. with velocity lying between c and c + dc. The number of molecules of a gas at rest as a whole which strike a unit area per unit time was shown by O. E. Myer to be equal to one-fourth of the number of molecules in the volume times the average velocity of the molecules. Thus, the number of molecules of mass m which strike unit area of the wire per second is one-fourth f(c)c dc, so the energy incident on the wire per unit area is

$$\tfrac{1}{2} m c^2 \times \tfrac{1}{4} f(c)\, c\, dc$$

Then the total energy for all velocities is

$$\frac{m}{8} \int_0^\infty f(c)\, c^3\, dc$$

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* Assume monatomic gas for the sake of simplicity. The effect of variable C_v is discussed later.

If the velocity distribution is Maxwellian, then

$$f(c) = \frac{4n}{\sqrt{\pi}} \left(\frac{m}{2kT_i}\right)^{3/2} e^{\frac{-mc^2}{2kT_i}} c^2$$

where n = number of molecules per c.c.

Substituting this into the above equation, we get for the total energy incident on the wire per second

$$E_i = n\left(\frac{2k^3 T_i^3}{\pi m}\right)^{1/2}$$

and for the number of molecules striking unit area of the wire per second, ν :

$$\nu = n\left(\frac{kT_i}{2\pi m}\right)^{1/2}$$

or since

$$p = nkT$$

where p is dynes/cm.^{2}

we may write

$$\nu = \frac{p}{\sqrt{2\pi m k T_i}}$$

which is Knudsen's Equation for the number of molecules which strike unit area per unit time.

Substituting ν into equation for E gives:

$$E_i = \nu \cdot 2kT_i$$

$$= \frac{p}{\sqrt{2\pi m k T_i}} \cdot 2kT_i$$

The assumption that the velocity distribution of the incident molecules is Maxwellian is valid because the molecules have all come into temperature equilibrium with the tubes before striking the wire. The molecules which leave the wire, however, do not necessarily come into temperature equilibrium with it, but instead have mean energy corresponding to T_r. Their velocity distribution will not be strictly Maxwellian but the departure from it decreases as $T_s - T_i$ becomes smaller. If we assume that the velocity distribution is Maxwellian, then the energy leaving the wire is

$$E_r = \nu \cdot 2kT_r$$

so the net loss of energy from the wire is

$$E_r - E_i = \frac{2pk}{\sqrt{2\pi m k T_i}} \left(T_r - T_i\right)$$

and since

$$\alpha \equiv \frac{T_r - T_i}{T_s - T_i}$$

then the net energy loss from the wire per $cm.^2$ per second is

$$\Delta E = \frac{2p\alpha k}{\sqrt{2\pi m k T_i}} \left(T_s - T_i\right) \qquad ergs/cm^2 - sec.$$

This is the equation given by Knudsen for the heat loss from a filament at low pressure. All the quantities except α may be measured, which then determines α.

As pointed out by Langmuir (5), the temperature of the re-emitted or reflected molecules has a clearly defined meaning only if the molecules leave the surface with a Maxwellian distribution of velocities. If the molecules do not come into thermal equilibrium, it is likely that the distribution will not be Maxwellian.

To avoid the ambiguity of the temperature T_r and to allow for large ΔT, where it is not Maxwellian, Langmuir defines the accommodation coefficient as the fraction of the theoretical heat loss (assuming temperature equilibrium) which is observed experimentally, i.e.:

$$\alpha = \frac{W_e}{W_T} \quad \text{where} \quad \begin{aligned} W_e &= \text{actual heat loss (no radiation)} \\ W_T &= \text{theoretical heat loss (no radiation)} \end{aligned}$$

The theoretical heat loss (i.e., assuming $\alpha = 1$) may be calculated as

$$\frac{W_T}{\pi d \ell} = \Delta E = \frac{p}{\sqrt{2\pi m k T_i}} \cdot 2k\left(T_s - T_i\right) \quad \text{ergs/cm}^2\text{-sec.}$$

so $$\alpha = \frac{W_e}{\Delta E \cdot \pi \ell d} = \frac{W_e \cdot \sqrt{2\pi m k T_i}}{p \pi \ell d \cdot 2k\,(T_s - T_i)}$$

If the gas is not monatomic, then the total energy of a molecule of the gas is

$$E = c_v T = \beta k T$$

Since the translational energy is 3/2 kT, the internal energy of a molecule of the gas is

internal = total - translational

It was shown previously that the total kinetic energy crossing a given surface is given by

$$E_i = \nu \cdot 2kT_i$$

so the kinetic energy crossing a given surface per molecule is

$$E_k = 2kT$$

and the internal plus kinetic energy per molecule crossing a given surface is

$$E_{TOTAL} = [(\beta - \tfrac{3}{2}) + 2k]T = (\beta + \tfrac{1}{2})kT$$

To get the maximum theoretical heat loss from the filament per molecule

$$E_f - E_b = k\int_{T_b}^{T_f} (\beta + \tfrac{1}{2})\,dT$$

Since the number of molecules hitting the filament is given by Knudsen's equation, then

$$\frac{W_T}{\pi \ell d} = \Delta E = \frac{p}{\sqrt{2\pi m k T_b}} \cdot k\int_{T_b}^{T_f} (\beta + \tfrac{1}{2})\,dT$$

so $$\alpha = \frac{W_e}{W_T} = \frac{W_e \cdot \sqrt{2\pi m k T_b}}{p \cdot \pi \ell d \cdot k\int_{T_b}^{T_f} (\beta + \tfrac{1}{2})\,dT}$$

where W_e = observed heat loss, ergs/sec.

m = mass of molecule, grams

p = pressure, dynes/cm.^{2}

βk = specific heat at constant volume per molecule

This equation was first used by Langmuir to determine the accommodation coefficient of hydrogen on tungsten.

Knudsen, in defining α, assumed it independent of pressure (in range where diameter of wire $<< \lambda$) and also independent of the temperature excess of the wire, provided the excess is small compared to temperature of the gas; i.e., for

$$\Delta T << T_{gas}$$

This is another way of saying that the velocity distribution of molecules leaving is approximately Maxwellian. It remained to be shown experimentally, however, that the above assumptions were valid. Using the equation for heat loss from the filament derived previously, Knudsen and others investigated the effect of surface conditions, different gases and metals, and various gas and wire temperatures on the accommodation coefficient. These effects will be discussed below.

Effect of Surface Conditions

The effect of the wire surface was determined by Knudsen by measuring α first on a smooth platinum surface, then on a surface slightly coated with platinum black, and finally on a surface heavily coated with platinum black. The increase in surface roughness gave rise to an increase in α. This experiment was carried out for several gases and the same trend noted. (See Table 1) (6)

TABLE 1

Platinum	α		
	H_2	O_2	CO_2
Polished	.358	.835	.868
Slightly Coated with Pt. Black	.556	.927	.945
Heavily Coated with Pt. Black	.712	.956	.975

Roberts (7), using a tungsten wire in a bulb containing helium at a pressure of about .10 mm Hg., observed a decided increase in α on prolonged heating of the wire. This he attributed to the increase in surface roughness resulting from heating the wire. For a clean filament--that is, one which had been flashed at a temperature of about 2000°C to remove adsorbed gases from the surface--the α increased from .07 to .18. For a filament with adsorbed gases on the surface the accommodation coefficient increased from .19 to .55.

It is reasonable that the increases in surface area which accompany increased surface roughness should allow greater exchange of energy of the gas molecules with the surface.

Roberts supposes an incoming molecule may strike in a "valley" of the surface and be reflected from one surface to another before leaving. Using this simple notion and the above data, Roberts derived an empirical expression which predicts the number of times a molecule should strike the surface to give the observed α. The concept of "molecularly rough" surface is sometimes useful--i.e., a surface which gives $\alpha = 1$. This is undoubtedly an oversimplified picture.

Probably a somewhat more realistic idea of what occurs is suggested by Langmuir in his adsorption theory of "definite sites" (8), of which a brief resume follows. The surface atoms of a solid are held to the atoms in the interior by forces similar to those acting between the atoms inside the solid. But in the surface layer, because of the asymmetry of the conditions, the arrangement must always be somewhat different from that in the interior. These surface atoms are unsaturated chemically and thus have a strong field of force surrounding them, the effective range usually less than the diameter of the molecule. Langmuir concluded, from other considerations, that when gas molecules strike a solid or liquid surface they condense on the surface due to the force field of the surface atoms and may later evaporate from it, but they do not, in general, rebound elastically. The length of time between condensation and evaporation depends on the intensity of the surface forces. If the forces are strong, evaporation will be slow and the surface of the solid will become saturated with a layer of the adsorbed gas. If the forces are weak, evaporation may occur so soon that only a small fraction of the surface will be covered at any instant. Since the range of the surface forces is small, the adsorbed molecules usually orient themselves in definite ways or on "definite sites", in the surface layer since they are held in position by forces acting between the surface atoms and particular atoms or groups of atoms in the molecule. It is apparent that the greater the surface area, the greater is the number of positions on the surface which are attractive to the incident molecules. Thus, more molecules will be condensed and evaporated per unit time, and the accommodation coefficient will be increased as a result of increasing the surface area.

As indicated above, the accommodation coefficient for a surface with a film of adsorbed gases is substantially larger than for a surface free from such a film. The latter condition (i.e., surface free from film) may be obtained by using a metal and a gas--for example, helium and platinum--which give rise to only weak surface forces so that the molecules which condense on the surface evaporate rapidly leaving only a small fraction of the surface covered by adsorbed molecules. Since it has been observed by Roberts (7), Mann (9), and others that the accommodation coefficient increases with time over the value for a clean surface, it may be assumed that the total surface covered by adsorbed molecules also increases with time so that a filament which has stood for a long period of time may finally get its surface completely covered by adsorbed molecules. Of course, the temperature of the surface and the pressure of the gas are important in determining the time required for this; if there are impurities in the gas, they will alter the situation also.

If the adsorption theory fits the physical situation, then one might eliminate the surface forces almost entirely by allowing a gas with chemical affinity for the solid to form a monolayer at the surface to chemically saturate the surface atoms. Then if some comparatively inert gas were admitted the surface forces originally causing condensation would be much smaller and evaporation would occur faster. Thus the molecules actually taking energy away from the surface (the inert gas) would not reside on the surface long enough to effect a very great energy transfer, and the accommodation coefficient would be expected to be quite small.

This appears to be borne out in several instances. Langmuir (5) measured an α of hydrogen on bare tungsten at a filament temperature of 1200° K and pressure of .20 mm Hg., and α dropped to .09 when the tungsten had an adsorbed film of oxygen on it. Later, Mann (9) noted that an oxygen treated platinum wire gave lower values of α with respect to helium than was obtained with pure helium. The accommodation coefficient for pure helium was about .05 and for oxygen-treated platinum, $\alpha = .035$.

Roberts (10) developed a method for measuring the adsorption of hydrogen on tungsten based on the fact that α of neon is different for a clean surface and for a surface with an adsorbed film of H_2 on it.

Since the adsorbed gases cause α to increase with time, the value of α for a clean filament is almost impossible to measure directly because of the lag from the time the gas is admitted to the bulb, to the time the readings are actually taken. The variation with time, however, can be made quite small by using very pure gas and operating at low pressures so that the rate of adsorption is quite slow. In this case, a linear extrapolation to zero time is possible. This method, unless variation with time is almost negligibly small, is open to objection on the grounds that the extrapolation is being made over a period when α is changing most rapidly. Some of the uncertainties may be removed by considering the process by which adsorption takes place. If we assume there are a certain number of available "sites" uniformly distributed over the surface of the filament, then the probability of capture of a gas atom in unit time is A_1.

where A_1 = number of unfilled sites on surface at any time t

A = total number of sites at $t = o$

So $$\frac{dA_1}{dt} = KA_1$$

and $$t = 1/K\left[\log A_1 + \log C\right]$$

Boundary conditions at $t = 0$, $A_1 = A_0$

So $$0 = 1/K\left[\log A_0 + \log C\right]$$

then $$t = 1/K \log \frac{A_1}{A_0}$$

In filling all the available sites A_0, α will change from the initial value α_0 to a final value α_∞; and in filling all of the available sites A_1 at time t, α varies from α to α_∞.

So we may write, $$K't = \log \frac{\alpha_\infty - \alpha}{\alpha_\infty - \alpha_0}$$

Since we may measure α_∞ and $\alpha(t)$, we may fit the exponential formula to the data to obtain α_0.

Michel (11), using data given in an early paper of Roberts (1930) in which α did not vary linearly with time, used this type formula to obtain α_0. The values obtained by this extrapolation did, in fact, agree with those obtained in later and better experiments by Roberts when the drift with time was negligibly small. Michel reports that, in practice, the linearity of the curve is extremely sensitive to the value of α_∞ and small adjustments of this quantity are sometimes necessary, but in no case tried thus far had it been necessary to use a value which departs more than 2 - 3% from that obtained after heat losses seemed reasonably steady--a limit well within the experimental accuracy.

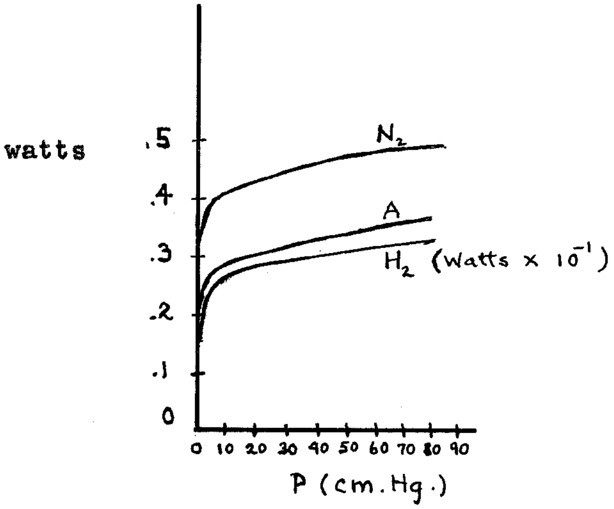
Effect of Pressure

Kinetic theory predicts that the amount of heat conducted away from a surface is independent of the pressure, provided the pressure is higher than the range in which "molecular flow" occurs. In the very low pressure range, however, where the mean free path of the molecules becomes significant compared to the relevant dimensions of the apparatus, careful measurements show that the thermal conductivity decreases linearly with pressure.

The following data of energy loss from a platinum filament, obtained by Dickens (12), shows that the heat conductivity is almost constant over a large range of pressures from about 10 to

76 cm., whereas below 5 cm. the thermal conductivity decreases linearly with pressure.

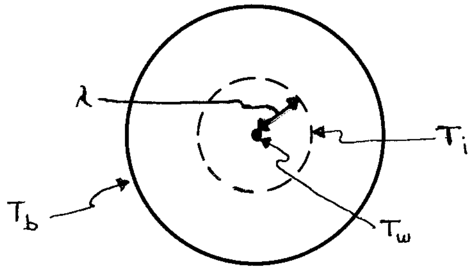
FIGURE 1.



For the range where the heat loss varies linearly with pressure, Knudsen's equation (previously derived) applies. If the heat loss were strictly linear with pressure, then the assumption of α independent of pressure would be completely valid. It must be shown experimentally, however, that this is the case. Mann, using .025 mm platinum wire in 5 cm. diameter bulb, investigated the range of pressures for which α should be independent of pressure and found the upper limit to be about 350 microns (for an accuracy of 2 - 3%).

Blodgett and Langmuir (5), in measuring α for hydrogen on tungsten at .2 mm Hg., corrected for the effects of conductivity between the gas molecules in the following way. The temperature of the impinging molecules was assumed to be the temperature of the molecules one mean free path length away from the filament, instead of the temperature of the bulb. (See Figure 2.)

FIGURE 2.



The temperature of these molecules was calculated using the ordinary laws of heat conduction through a gas. This correction made about a five percent change in the value of α based on assuming the temperature of the impinging molecules the same as the temperature of the bulb. This correction becomes smaller as the λ increases (or pressure decreases).

Effect of Temperature

In determining the effect on the accommodation coefficient of varying the temperature of the wire and the gas, care must be taken that the assumptions made in defining α are not violated. That is, if the accommodation coefficient as defined by Knudsen is used, then in order to assure that the gas leaves the wire with approximately a Maxwellian distribution of velocities, the temperature difference must be kept small. This requires that the wire temperature be maintained about 20-30° above the bulb temperature. So, to get α as a function of temperature, the bulb temperature must be varied and the wire temperature maintained at a value somewhat larger. This technique was used by Knudsen and Roberts. The bulb was submerged in a constant temperature bath of ice and water at 0°C, dry ice at -80°C, and liquid N_2 at -192°C. The results are given in Table 2 below.

TABLE 2.

Knudsen using a "fine wire" on He.:		Roberts using W on He.:	
T		T	
0°C	.35	0°C	.057
-80°C	.376	-80°C	.047
-192°C	.423	-192°C	.025

The above method of obtaining the temperature dependence of the accommodation coefficient is somewhat less convenient to use than a method which will allow the wire temperature to vary while holding the bulb temperature constant (i.e., varying ΔT).

Langmuir's definition of α avoids the small ΔT restriction. The accommodation coefficient versus temperature curve for hydrogen on tungsten, using the above definition, was obtained by Langmuir. The gas temperature varies even though the bulb temperature is constant because the gas temperature is taken to be the temperature one mean free path away from the filament (p = .2 mm Hg.). See Table 3, below. (5)

TABLE 3.

T_w (°K)	T_b	α
150	86	.195
300	96	.151
500	109	.153
700	130	.222
900	160	.354
1100	192	.500
1400	216	.537
1600	276	.519

Mann (9) determined accommodation coefficients for helium and argon on platinum, using Knudsen's equation over a range of wire temperature from 100°C to 1000°C (i.e., large ΔT). Gas pressures of about .35 mm Hg. were used and noticeable change of α with time was observed. For bulb at room temperature, α for argon varied from .55 to .35 as wire changed from 100°C. to 1000°C. Helium at room temperature was obtained by extrapolating α versus time curve to zero time. Values ranged from .045 to .07 at wire temperature between 100°C to 1000°C. The exchange of energy between gas molecules and surface molecules of a solid depends, as indicated previously, on the conditions at the surface (including smoothness and chemical affinity of surface molecules and gas molecules) on the temperature and pressure of the gas, on the temperature of the filament, and on the molecular weight of the gas and surface molecules. One might expect that, other conditions being the same, the gas with the higher molecular weight would have the higher accommodation coefficient. This, generally speaking, is the case. The accommodation coefficients for various gases and metals determined from Knudsen's equation for small ΔT are tabulated in Table 4.

TABLE 4.

Gas	Metal	Temp.	Surface Condition	α	Ref.
Hydrogen	Platinum	0°C	Polished Not Flashed	.358	(6)
Hydrogen	Tungsten	20°C	—	.20	(2)
Helium	Nickel	20°C	Not Flashed	.20	(7)
Helium	Nickel	20°C	Flashed	.085	(7)
Helium	Tungsten	0°C	Polished Not Flashed	.19-.55	(7)
Helium	Tungsten	0°C	Flashed	.07-.18	(7)
Helium	Tungsten	20°C	Flashed	.17	(13)
Helium	Tungsten	20°C	Not Flashed	.53	(13)
Nitrogen	Tungsten	20°C	—	.57	(2)
Argon	Tungsten	20°C	—	.85	(2)
Argon	Tungsten	20°C	Flashed	.82	(13)
Argon	Tungsten	20°C	Not Flashed	1.0	(13)

DESCRIPTION OF APPARATUS

Vacuum System:

In order to accurately measure the heat loss from a filament due to the presence of a gas alone, the effects of heat loss due to radiation and conduction along the leads must be carefully determined. This can best be done by measuring directly this loss in a good vacuum. This vacuum is obtained by using a three-stage oil diffusion pump which evacuates the bulb in which the filament is placed to a pressure of approximately 10^{-7} mm Hg. as indicated by an ionization gauge located in the system. (See Figure 3)

The gases for which the accommodation coefficients are desired are contained in bulbs fused directly into the vacuum system, so that no contamination due to leaks in connections or dirty tubing is possible. To facilitate admitting a desired pressure of gas into the bulb a Pirani gauge is used which gives the instantaneous pressure in the system. This gauge gives a good estimate of the pressure in the bulb, but at low pressures (of the order of 50 microns) the reading is not sufficiently accurate to use in the actual calculation of α. For this purpose a McLeod gauge which measures the absolute pressure (i.e., does not need to be calibrated, as the Pirani does) is used.

Electrical System:

To obtain accommodation coefficients as a function of temperature,

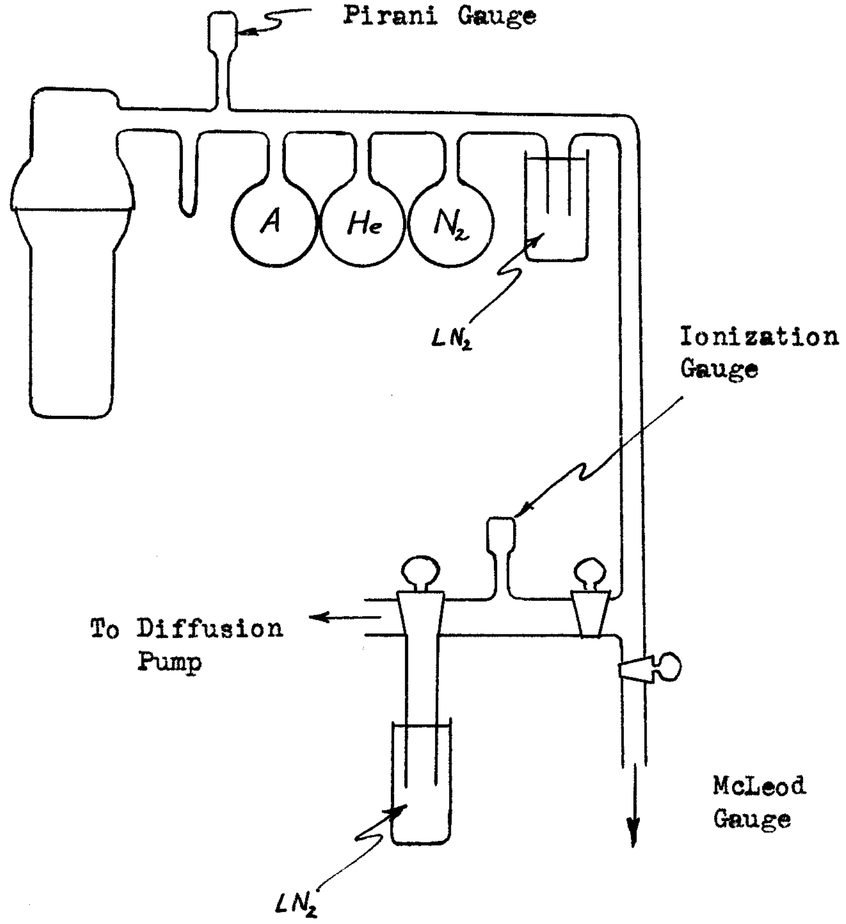

Pirani Gauge
A
He
N_2
LN_2
Ionization Gauge
To Diffusion Pump
McLeod Gauge
LN_2

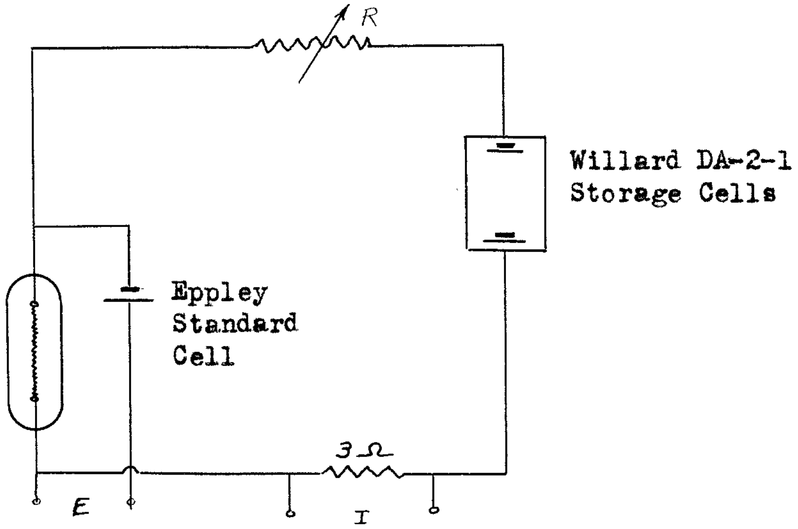
FIGURE 3.

it is necessary to measure the power supplied to the filament at various filament temperatures. Since the temperature of a given wire is uniquely determined by the resistance, we need also to measure the resistance at each power input setting. Both resistance and power are determined by current and voltage.

The current is supplied to the filament by Willard DA-2-1 storage cells chosen for their ability to give essentially constant voltage under low amperage operating conditions. The current through the filament is determined by measuring the voltage drop across a precision 3-ohm resistor (accurate to ± .05 percent) with a Rubicon precision potentiometer. This same potentiometer is used to measure the voltage drop across the filament itself. Since the upper limit on the potentiometer is 1.61 volts, an Eppley Standard Cell is placed in series with the potentiometer and is used to oppose or "buck out" the voltage across the filament when that voltage exceeds the potentiometer range.

The voltage applied to the filament may be adjusted by varying the resistance in series with the filament. The power and resistance of the filament may be measured at all times to an accuracy of .5% or better. (See Figure below).

FIGURE 4.



Filaments and Gases

Tungsten and platinum filaments of the pure metal were obtained from the Sigmund Cohn Company. The diameter of the tungsten is .001 inches and of the platinum is .00125 inches. The length of the filament varies from one experiment to the next, and measurement was made after each experiment since the length changed somewhat due to heating. The tungsten filament was "aged" by heating to approximately 2800°K in vacuum for fifteen minutes.

The gases were obtained from the Air Reduction Company in one liter glass flasks. Nitrogen and helium are 100% pure (i.e., no impurities are detectable up to the limit of mass spectrometer) and the only impurity in the argon is .015% nitrogen.

EXPERIMENTAL METHOD

It was desired to determine the accommodation coefficient as a function of temperature for a clean filament; that is, one which is free from any adsorbed gases. Since the rate of adsorption varies directly with pressure and inversely with temperature, the lower the pressure used and the higher the filament temperature used, the slower will be the rate of adsorption of the gas on the filament. In fact, it may be possible to reach a steady-state where the molecules which condense on the surface evaporate so quickly that there is practically no adsorbed film formed.

With this idea in mind, it was decided to operate at as low pressures as possible. The lower limit was determined by the necessity of making the power change large enough to give reasonable accuracy to the calculations of α. Since the radiation heat loss becomes quite large at high temperature, and the power loss due to gas is obtained by subtracting the radiation heat loss from the total heat loss, it was necessary to use pressures of about 50 microns (.05 mm Hg.) to make the net loss large enough to determine accurately. At this pressure, there was no perceptible change with time in the readings of either the current through the wire or the voltage drop across it.

That is, the gas was admitted to the bulb and measurements were made within one minute and were continued at intervals of two minutes for the next ten to fifteen minutes with no change detectable within the accuracy of the potentiometer.

As a check to determine whether any water vapor from the main portion of the system was reaching the bulb, a liquid nitrogen trap was placed in the line immediately before the entrance to the bulb. The readings were the same whether the trap was present or not, indicating no impurities were reaching the bulb from other parts of the system.

To determine the accommodation coefficient the following procedure was used:

(a) A filament was fastened into position in the bulb and the bulb evacuated to approximately 10^{-7} mm Hg.

(b) The filament was then heated to a high temperature to remove any surface impurities.
    (1) Tungsten heated to 2000°K for about five minutes.
    (2) Platinum heated to about 1800°K for five minutes.

(c) Current and voltage measurements were made over a range of filament temperatures from about bulb temperature to approximately 1000°C above it (actual range varied with filament)

(d) Gas was admitted to approximately 50 microns pressure and measurements repeated over the same temperature range.

(e) Bulb temperature was varied by immersing in a liquid nitrogen bath (80°K) and a CO_2 and acetone bath (193°K), and variation with filament temperature again determined.

CALCULATION OF ACCOMMODATION COEFFICIENT

Since the temperature difference between filament and bulb is varied to obtain the dependence of the accommodation coefficient upon temperature, the definition of α as given by Langmuir was used, as it is not necessary that ΔT be small.

$$\alpha = \frac{\Delta W}{W_T} = \frac{\Delta W \sqrt{2\pi m k T_b}}{k\left[\int_{T_b}^{T_f} (\beta + \tfrac{1}{2})\, dt\right] \cdot p \pi l d}$$

where $\Delta W =$ (observed - radiation) heat loss, ergs/sec.

m = mass of molecule, gms.

k = Boltzman's constant, 1.371×10^{-16} ergs/°K

p = pressure, dynes/cm.^{2}

d = filament diameter, cm.

βk = specific heat at constant volume/molecule, ergs/°K

l = length of filament, cm.

For monatomic gases such as argon and helium, $\beta = 3/2$, so we may write:

$$\alpha = \frac{\Delta W \sqrt{2\pi m k T_b}}{2k(T_f - T_b) p \pi l d}$$

so for m(argon) = 6.631×10^{-23} gm./molecule

m(helium) = $.665 \times 10^{-23}$ gm./molecule

and converting p to mm Hg. and ergs/second to watts, we have

$$\alpha_A = 2.08 \left\{ \frac{T_b^{1/2} \Delta W}{l d p (T_w - T_b)} \right\}$$

$$\alpha_{He} = .660 \left\{ \frac{T_b^{1/2}\, \Delta W}{l\, d\, p\, (T_w - T_b)} \right\}$$

for nitrogen, $m = 4.652 \times 10^{-23}$ gm./molecule

$$\alpha_{N_2} = 3.47 \left\{ \frac{T_b^{1/2}\, \Delta W}{l\, d\, p\, [(\beta_w + 1/2) T_w - (\beta_b + 1/2) T_b]} \right\}$$

T_b = bulb temperature, °K

T_w = filament temperature, °K

ΔW = (total - radiation) heat loss, watts

p = pressure, mm Hg.

d = diameter of filament, cm.

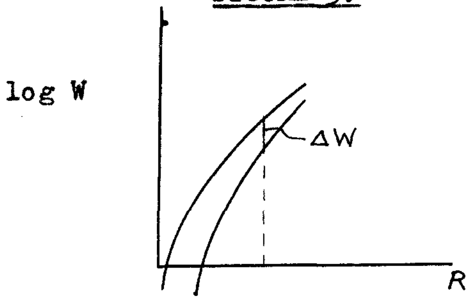
l = length of filament, cm.

β = pure number

(βk = specific heat at constant volume/molecule)

From the measurements of E and I of the filament in a vacuum, a curve of power (EI) versus resistance (E/I) was plotted. A similar plot was made for power and resistance of the filament with the gas present. The ΔW was obtained by taking the difference of the two curves at the same resistance, or temperature. (See Figure 5.)

FIGURE 5.



From the literature, curves of resistivity versus temperature are available for pure tungsten and platinum. Since the dimensions of the filament are known and the resistance for any given power setting is known, the resistivity may be determined, and from this the temperature obtained.

As the leads to which the filament is attached are much larger than the filament, they remain at a much lower temperature than the filament. The leads then cool the ends of the filament and thus lower its resistance. If the overall resistance of the filament is measured, it corresponds only to some average temperature of the filament. Langmuir found that for a three mil tungsten wire at a maximum temperature of 1000°K., 18 percent of the filament has a temperature 20° or more below the temperature at the center; at a maximum temperature of 800°K., 27 percent was 20° or more below maximum; and at 600°K., 48.7 percent was 20° or more below maximum. Since the temperature is not uniform, an average temperature is used—one which corresponds to the measured resistance.

RESULTS

The apparatus was originally set up to measure accommodation coefficients as a function of temperature by maintaining the temperature of the incident gas constant at 300° K. and increasing the filament temperature from a value near 300° K. to approximately 1000° K. The results of these experiments for helium, argon, and nitrogen on platinum and tungsten are given in Figures 6 and 7.

All of the curves show the same behavior in the low filament temperature range, i.e., a rapid rise in α to a maximum at a ΔT of between 25° and 75° and a decrease as the filament temperature is increased.

In order to determine if this peak was dependent on the actual filament temperature or on the difference between filament temperature and bulb temperature, the bulb was immersed in liquid nitrogen which facilitated an increase in ΔT at a given filament temperature. The results of lowering T_b to 80° K. on the accommodation coefficient of helium, argon, and nitrogen on tungsten are indicated in Figures 8, 9, 10. The effect, in general, was to lower the absolute magnitude of α in the direction of increased ΔT. The general shape of the curves, however, persists. This trend with ΔT has not been reported in the literature, possibly because previous investigators have been concerned with maintaining as small a ΔT as possible, consistent with reasonable accuracy, rather than determining the effect of temperature difference.

While Roberts (7) reports no variation with ΔT, he does report a sharp rise in α due to "prolonged heating" which, however, he states is "undoubtedly due to increased surface roughness".

It is difficult to compare these data obtained in this report with values reported in the literature because the reported values in general do not specify at what ΔT they were obtained.

Roberts, in determining the accommodation coefficient of helium on tungsten, uses a ΔT of "10 or 20°" and reports values of .07 to .18. If the curve of α versus ΔT (for $T_b = 300°K.$) is extrapolated to this ΔT range, the values obtained are in agreement with Roberts' values.

Michel reports an accommodation coefficient for argon on tungsten of .82 with ΔT unspecified. This value may also be checked by choosing a value of ΔT of about 20° from Figure 9.

The value of .57 given for nitrogen on tungsten by Langmuir is neither confirmed nor denied by the present data, since the temperature at which the value was obtained is not given.

From the shape of the α versus ΔT curves, it appears that if the curves were extrapolated to $\Delta T \approx 0$, the accommodation coefficient obtained would be zero. However, the theory developed by Lennard-Jones and his coworkers sheds some light on the expected values at $\Delta T \rightarrow 0$, since the definition of α is taken as

$$\alpha = \lim T_1 \rightarrow T_2 \rightarrow T \quad \frac{T_2' - T_1}{T_2 - T_1}$$

Devonshire (1), using the above definition and assuming that the potential energy between the solid and gas atoms is given by a Morse function, obtains a general expression for α in terms of the constants of the gas and metal. This he evaluated for the simple case of helium on tungsten. The values obtained for T = 297° K. and T = 80° K. are approximately .055 and .025, respectively.

If the curves in Figure 8 (for helium on tungsten at $T_b = 300°$ K. and $T_b = 80°$ K) are extrapolated to $\Delta T = 0$, the values of α obtained by the theory appear as reasonable intercepts.

So the theory, while it does not predict the variation of α with ΔT, does indicate that as $\Delta T \rightarrow 0$ the accommodation coefficient becomes very small but remains finite.

To determine accurately filament temperatures below 273° K., the resistance of the tungsten filament was measured at 80° K. by submerging the filament itself in liquid nitrogen. This then established the temperature versus resistivity curve for the low temperature range, so that intermediate values could be interpolated. (See Figure 11)

When the bulb was placed in liquid nitrogen the electrical leads which were located at the top of the bulb were not immersed, so reached an equilibrium temperature between 300° K. and 80° K. Ideally, of course, both bulb and leads should have been at the same temperature, but the design of the apparatus was such that this was impossible. Thus, the filament when placed in a vacuum with the bulb in liquid nitrogen reached an equilibrium temperature of 255° K. When the gas was admitted, heat was conducted away from the filament by the gas and the filament reached a temperature some 100° or so lower.

So, the values of α obtained in the low ΔT range with liquid nitrogen are open to question because of the uncertainty of the amount of heat added to the filament due to conduction through the leads. The electrical power required to give a particular filament temperature was undoubtedly less than would have been required had the filament been at the same temperature as the bulb before heating was begun.

This difficulty was, of course, not encountered when the bulb was at room temperature because both filament and bulb were initially at the same temperature. It is significant to note, however, that the power required versus temperature curve has the same shape whether the bulb is at room temperature or at 80° K., and this strongly suggests that α will also follow the same general curve at the two bulb temperatures, since the other factors determining α do not change significantly with temperature.

There is one exception, however, in the similarity of the shape of the power required versus temperature curves at the two bulb temperatures, and that is the case of helium. (See Figure 15) As the filament temperature is increased, the power required increases smoothly until a temperature of approximately 230° K. is reached (corresponding to segment a-b of Figure 15.), at which time the filament temperature rapidly rises to a temperature of approximately 575° K. with no change of the control rheostat (b-c). At this new point of equilibrium it is possible to decrease the temperature to approximately 300° K. (c-d), at which time another rapid change occurs with no change in control rheostat, the filament temperature finally reaching a value of approximately 150° K. (d-e).

It might immediately be suspected that this peculiar behavior is due to the fact that the equilibrium filament temperature when no current is flowing is not the same as the temperature of the bulb walls. But the other gases--argon and nitrogen--exhibited a smooth and continuous power versus temperature relation in the same apparatus at low bulb temperature. The effect of this discontinuity on the accommodation coefficient may be seen in Figure 8. The same procedure was carried out with a pressure more than four times as great as the original pressure and the same sort of discontinuity noted; the "jump" occurred, however, at a somewhat lower temperature.

The pressure in the bulb when the bulb was immersed in liquid nitrogen was difficult to measure because the bulb and the McLeod Gauge were not at the same temperature. When the mean free path in the bulb is large compared with the dimensions of the connecting tubing, one may use the relation

$$\frac{p_{bulb}}{p_{gage}} = \sqrt{\frac{T_{bulb}}{T_{gage}}}$$

as shown from kinetic theory. When the mean free path is small compared to the connecting tubing, then the pressure reading on the McLeod Gauge is the true pressure throughout the system.

However, in the transition region when the mean free path is of the same order as the internal dimensions of the connecting tubing, no such simple relationship exists. Unfortunately, this transition range is the one of interest in the present low temperature experiments, since the mean free path of, say, nitrogen at about 50 microns is of the order of .1 cm. and the minimum diameter of connecting tube is approximately .2 cm.

Knudsen has shown theoretically that in this range the pressure gradient is a function of tube diameter and pressure in the hot chamber (i.e., independent of molecular weight). Experimental values of the ratio of bulb pressure to gauge pressure in the transition range when the bulb was at 90° K. and the gauge at 298° K. have been determined by Tomkins and Wheeler (8) for hydrogen. These ratios were used to determine the bulb pressure in the present experiments since the gauge pressure was known.

It was of interest to determine the effect of varying the bulb temperature while holding the filament temperature constant (See Figure 18). This was done at high ΔT where the values obtained are more reliable. Three bulb temperatures were used, 80° K. (liquid nitrogen), 190° K. (solid CO_2 and acetone) and 300° K. (room temperature). In calculating α the square root of the bulb temperature is used, so α was plotted versus the square root of the bulb temperature.

That α is approximately proportional to the square root of the molecular weight at constant temperature (for the gases tested) is shown in Figure 19.

CONCLUSIONS

In order to properly specify the accommodation coefficient of a particular gas on a given surface, the actual temperature of both the incident gas and the surface must be known, as well as the condition of the surface. Values of α with no temperature specification are inadequate, judging from the results of these experiments.

In general, the accommodation coefficient varies quite rapidly in the small ΔT range, reaching a maximum at a ΔT between 25 and 75° and then decreasing as the temperature difference is increased.

The variation of α with temperature is a smoothly continuous one for all gases and metals tested, with the notable exception of helium and tungsten at a gas temperature of 80° K., which shows a sharp break from $\alpha_{max.}$ to a value considerably less than maximum α. The temperature at which this break occurs decreases somewhat with increased pressure.

The platinum filament gave more nearly constant values of α in the large ΔT range than did tungsten for the gases tested.

In general, the accommodation coefficient was observed to increase with increase in the molecular weight of the gas; the effect of pressure on α (up to 150 microns) was negligible.

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ACCOMMODATION COEFFICIENT, α
VERSUS FILAMENT TEMPERATURE, T_w

BULB TEMPERATURE = 300 °K
SURFACE — PLATINUM
○ HELIUM
△ ARGON
□ NITROGEN

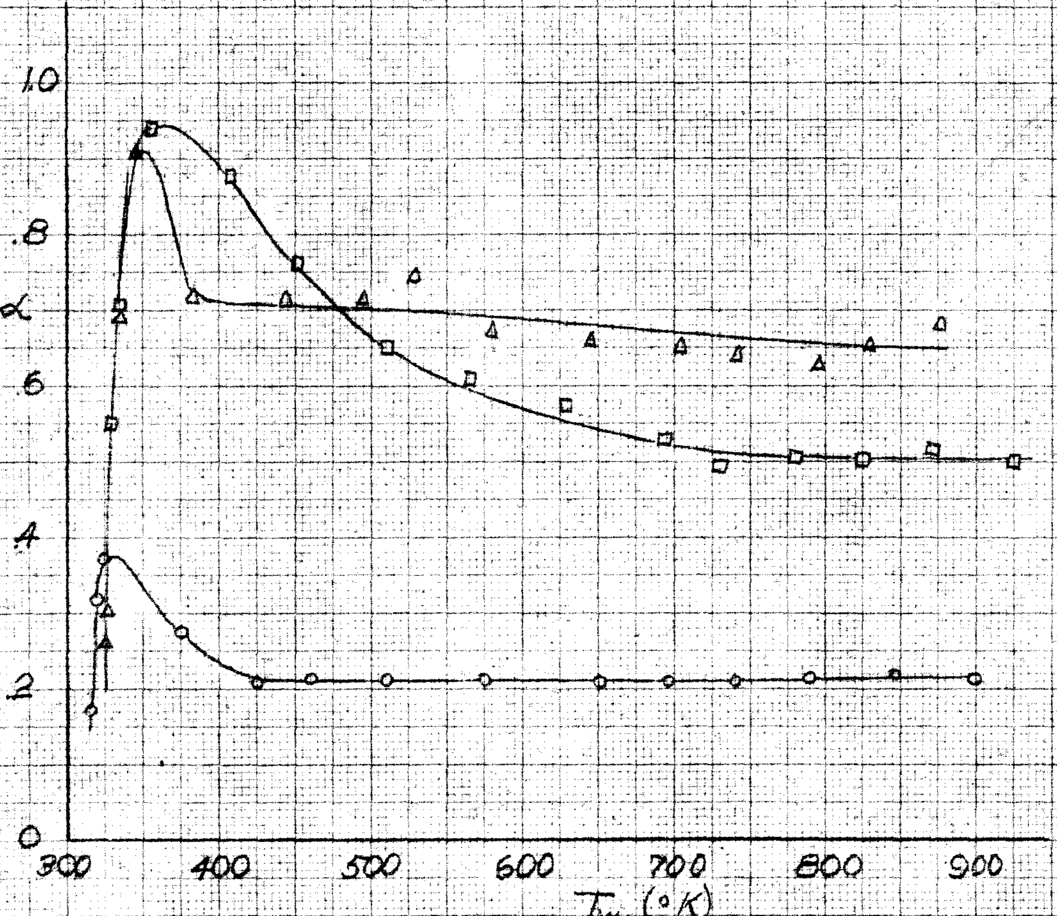


FIGURE 6

ACCOMMODATION COEFFICIENT, α
VERSUS FILAMENT TEMPERATURE, T_w

BULB TEMPERATURE = 300 °K
SURFACE – TUNGSTEN
⊙ HELIUM
△ ARGON
□ NITROGEN

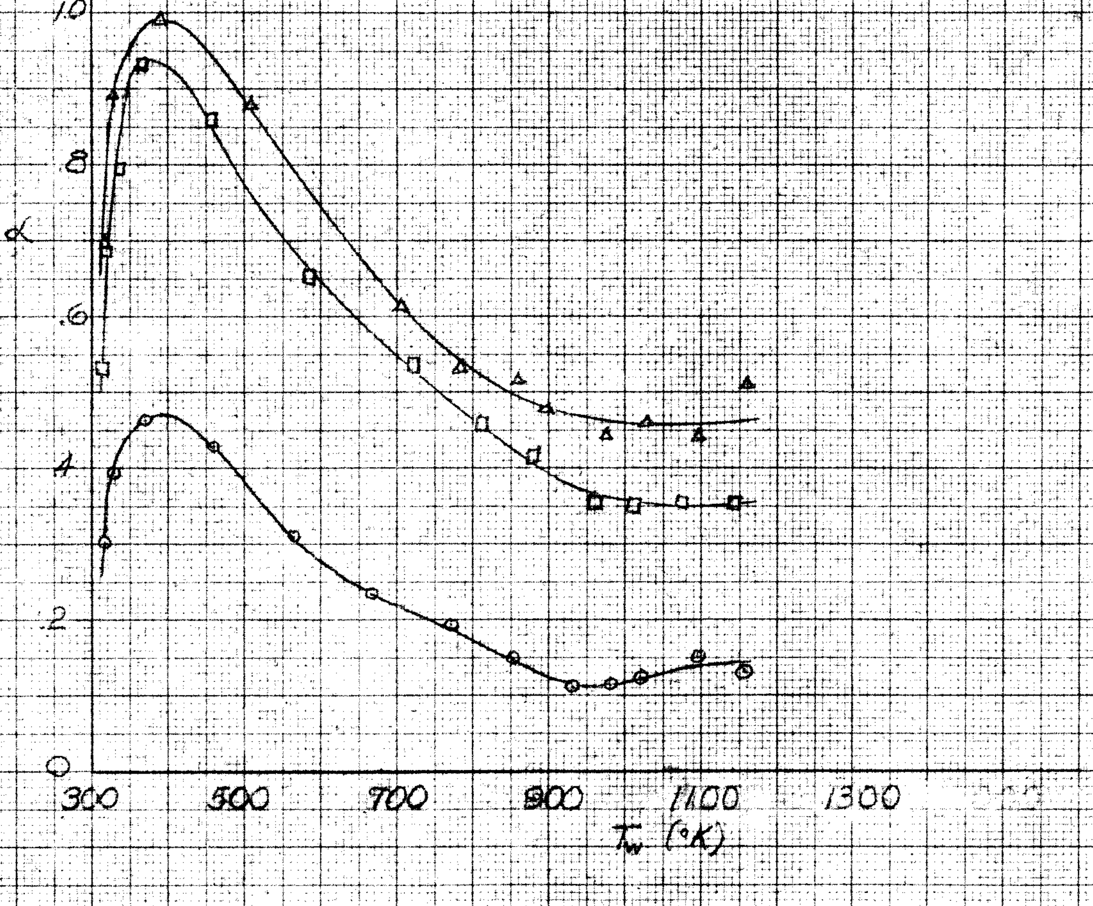


FIGURE 7

ACCOMMODATION COEFFICIENT, α
VERSUS TEMPERATURE DIFFERENCE $(T_W - T_B)$
FOR HELIUM ON TUNGSTEN

○ BULB TEMPERATURE = 80°K
△ BULB TEMPERATURE = 300°K

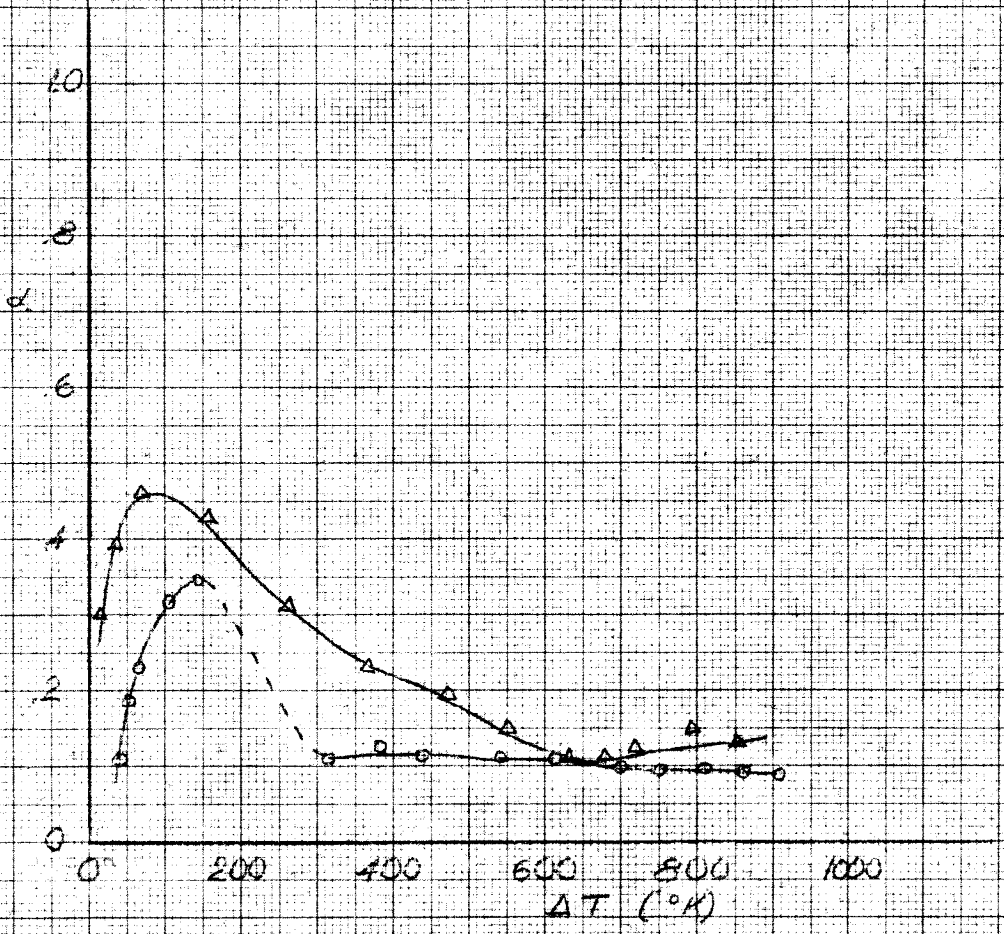


FIGURE 8

ACCOMMODATION COEFFICIENT, α
VERSUS TEMPERATURE DIFFERENCE $(T_W - T_B)$
FOR ARGON ON TUNGSTEN

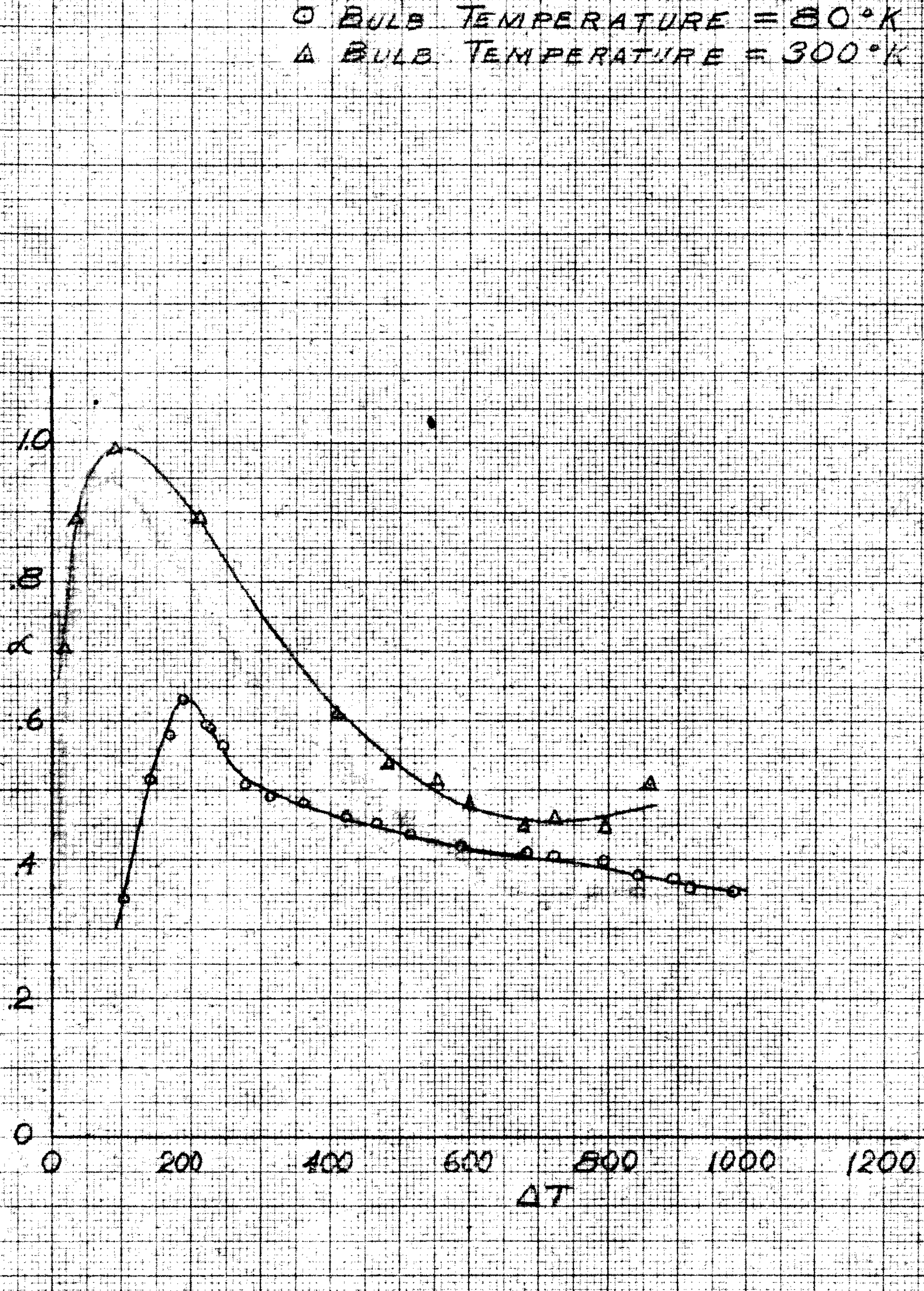


FIGURE 9

ACCOMMODATION COEFFICIENT, α
VERSUS TEMPERATURE DIFFERENCE $(T_w - T_b)$
FOR NITROGEN ON TUNGSTEN

⊙ BULB TEMPERATURE = 80°K
△ BULB TEMPERATURE = 300°K

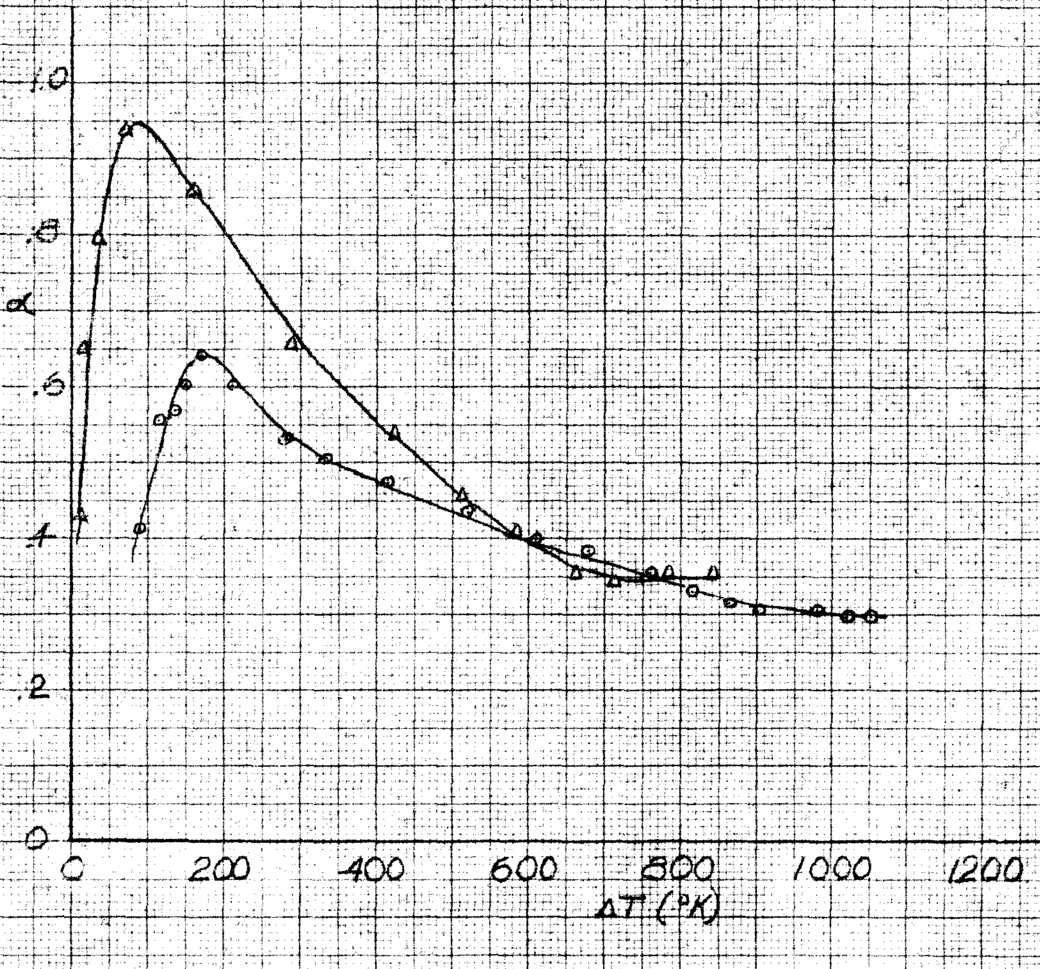
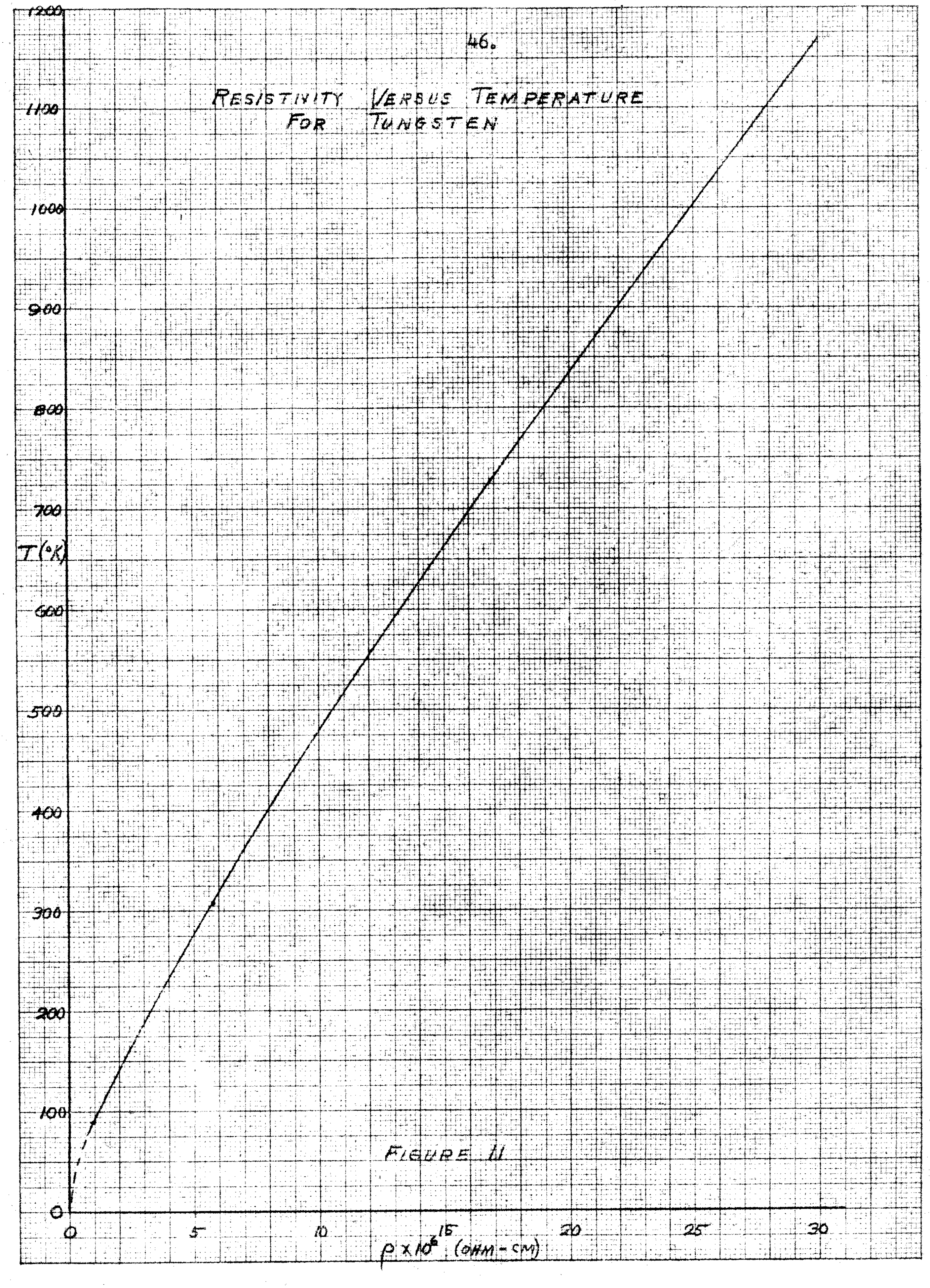
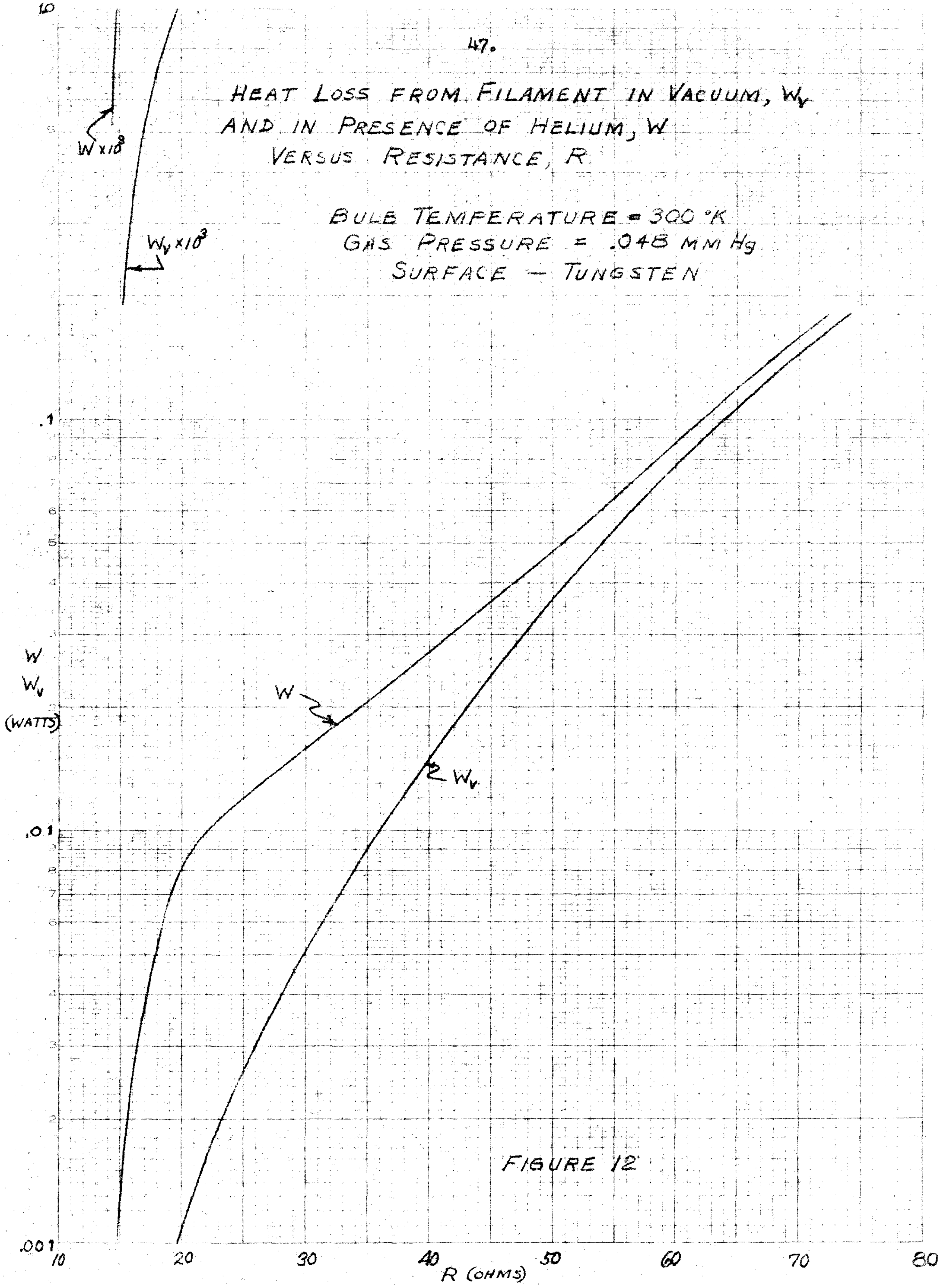


FIGURE 10



RESISTIVITY VERSUS TEMPERATURE FOR TUNGSTEN

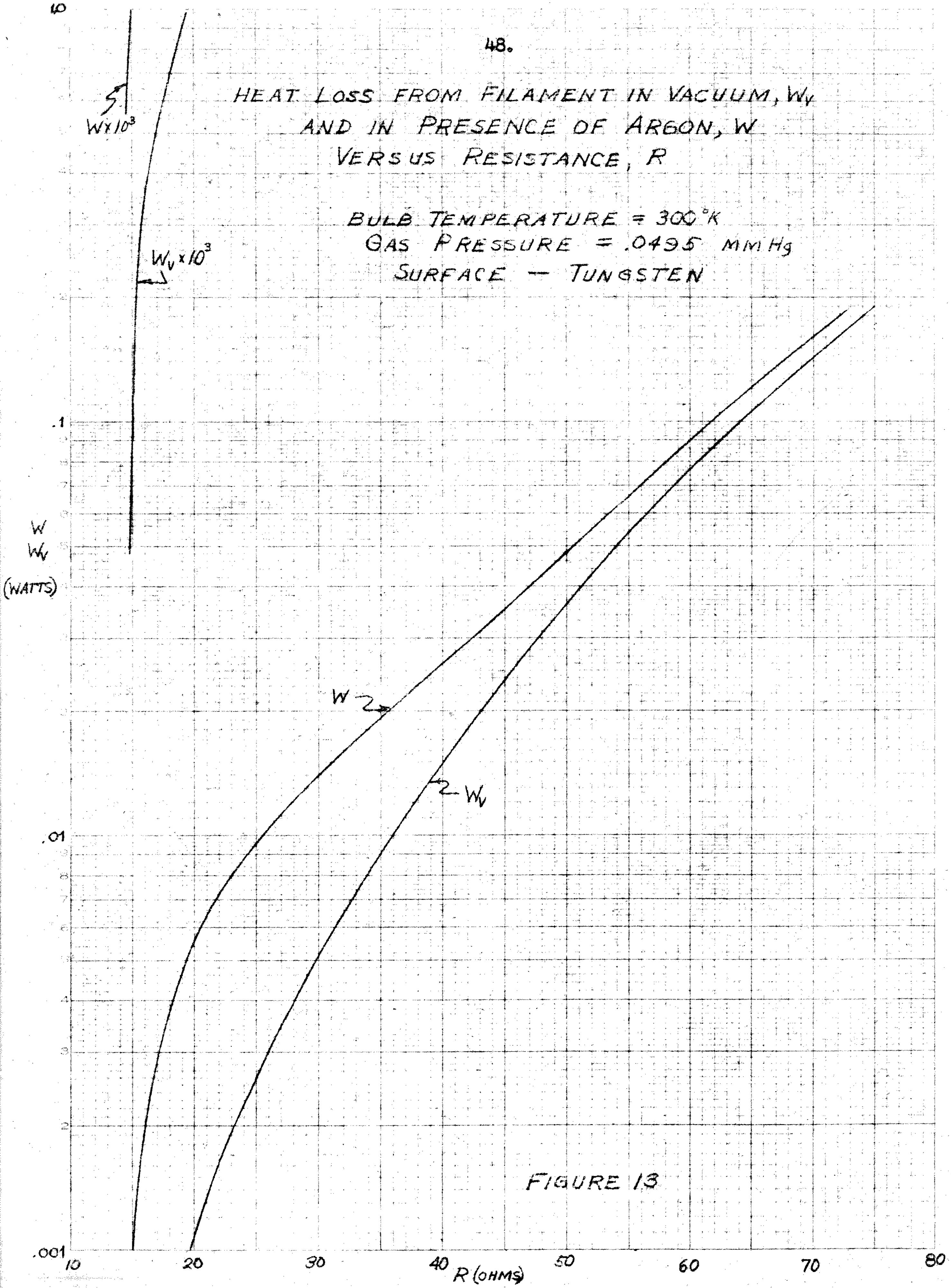
FIGURE 11



HEAT LOSS FROM FILAMENT IN VACUUM, W_v
AND IN PRESENCE OF HELIUM, W
VERSUS RESISTANCE, R

BULB TEMPERATURE = 300 °K
GAS PRESSURE = .048 MM Hg
SURFACE — TUNGSTEN

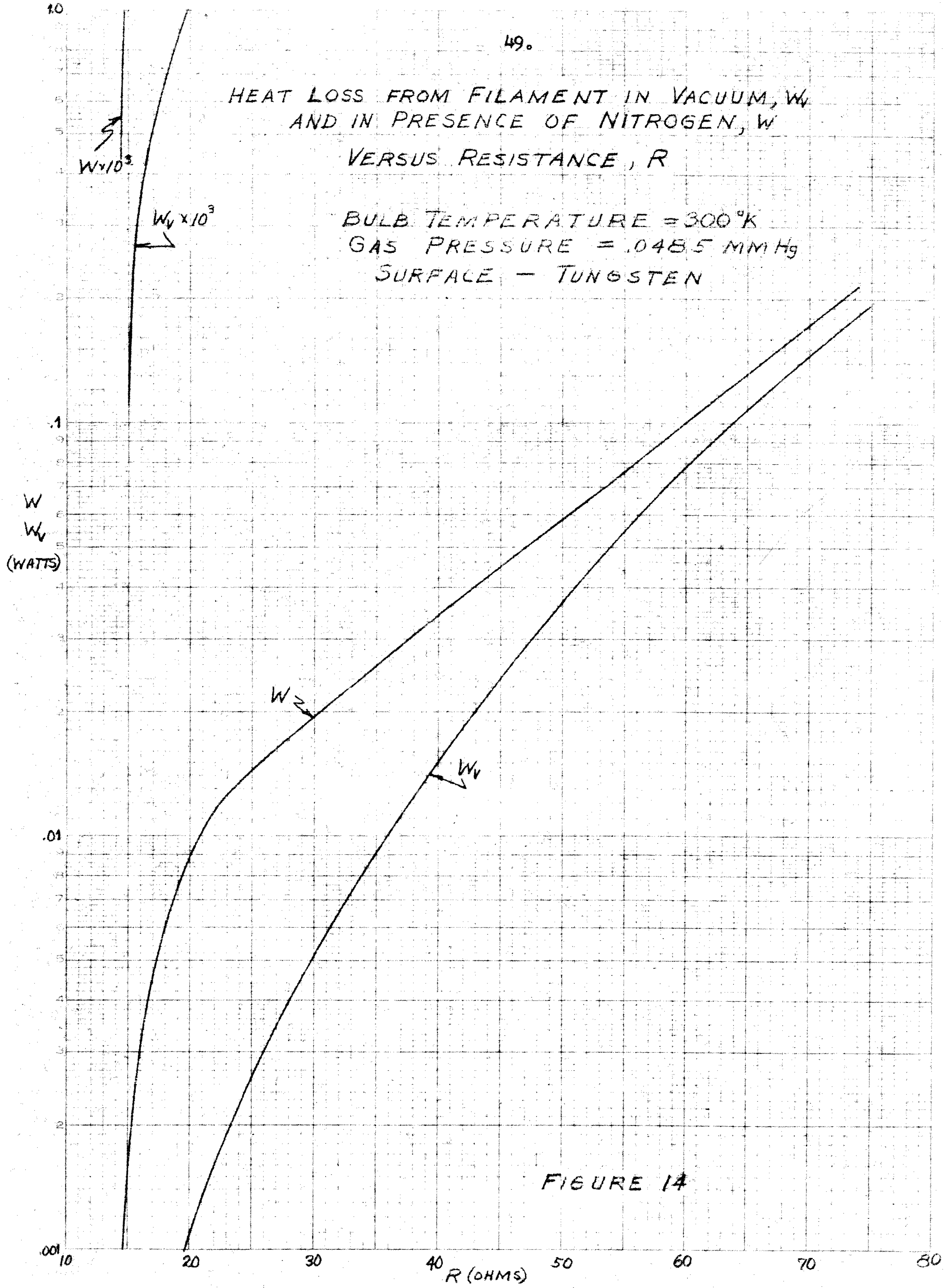
FIGURE 12



HEAT LOSS FROM FILAMENT IN VACUUM, W_V
AND IN PRESENCE OF ARGON, W
VERSUS RESISTANCE, R

BULB TEMPERATURE = 300°K
GAS PRESSURE = .0495 MM Hg
SURFACE — TUNGSTEN

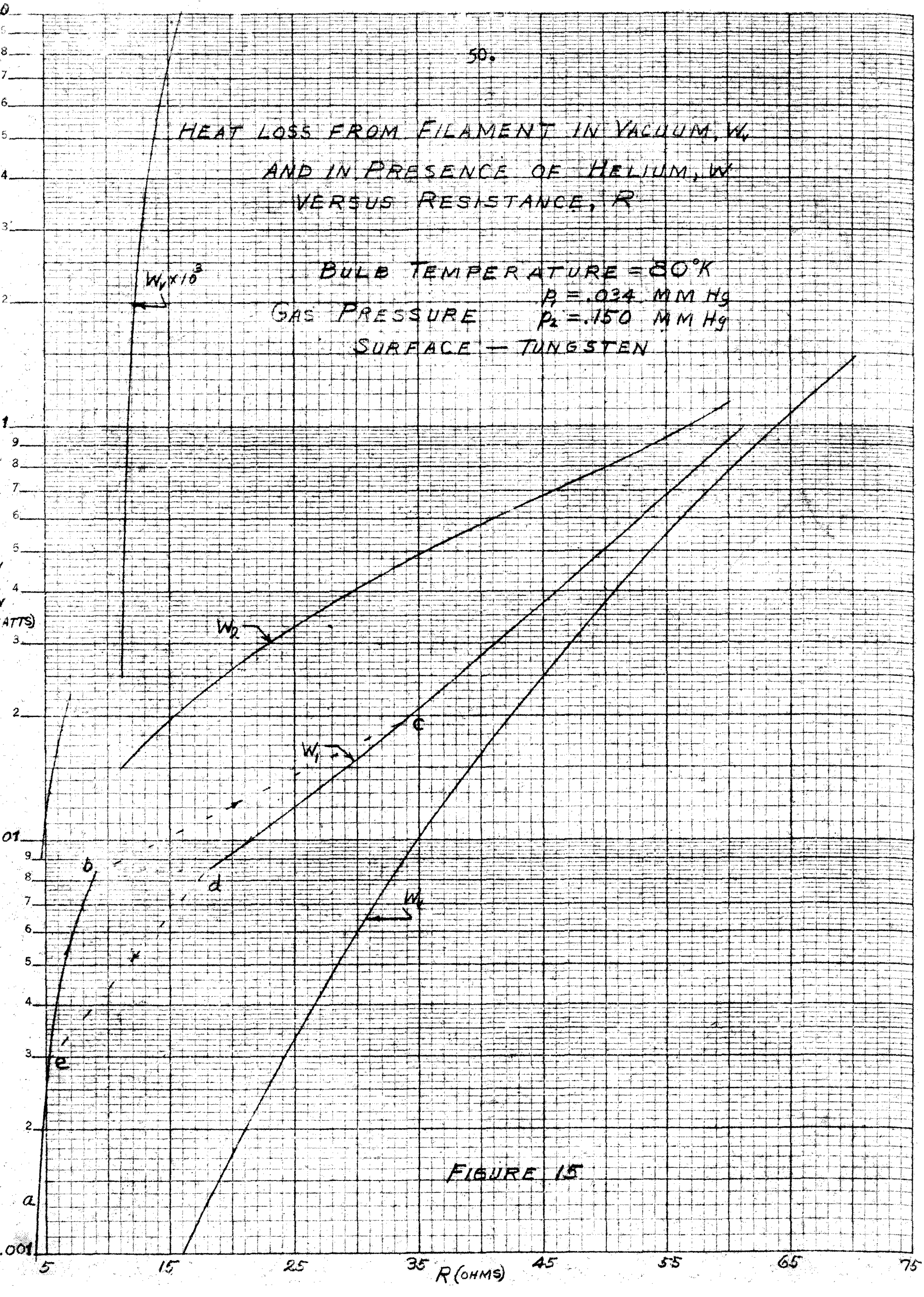
FIGURE 13



HEAT LOSS FROM FILAMENT IN VACUUM, W_V
AND IN PRESENCE OF NITROGEN, W
VERSUS RESISTANCE, R

BULB TEMPERATURE = 300°K
GAS PRESSURE = .0485 MM Hg
SURFACE – TUNGSTEN

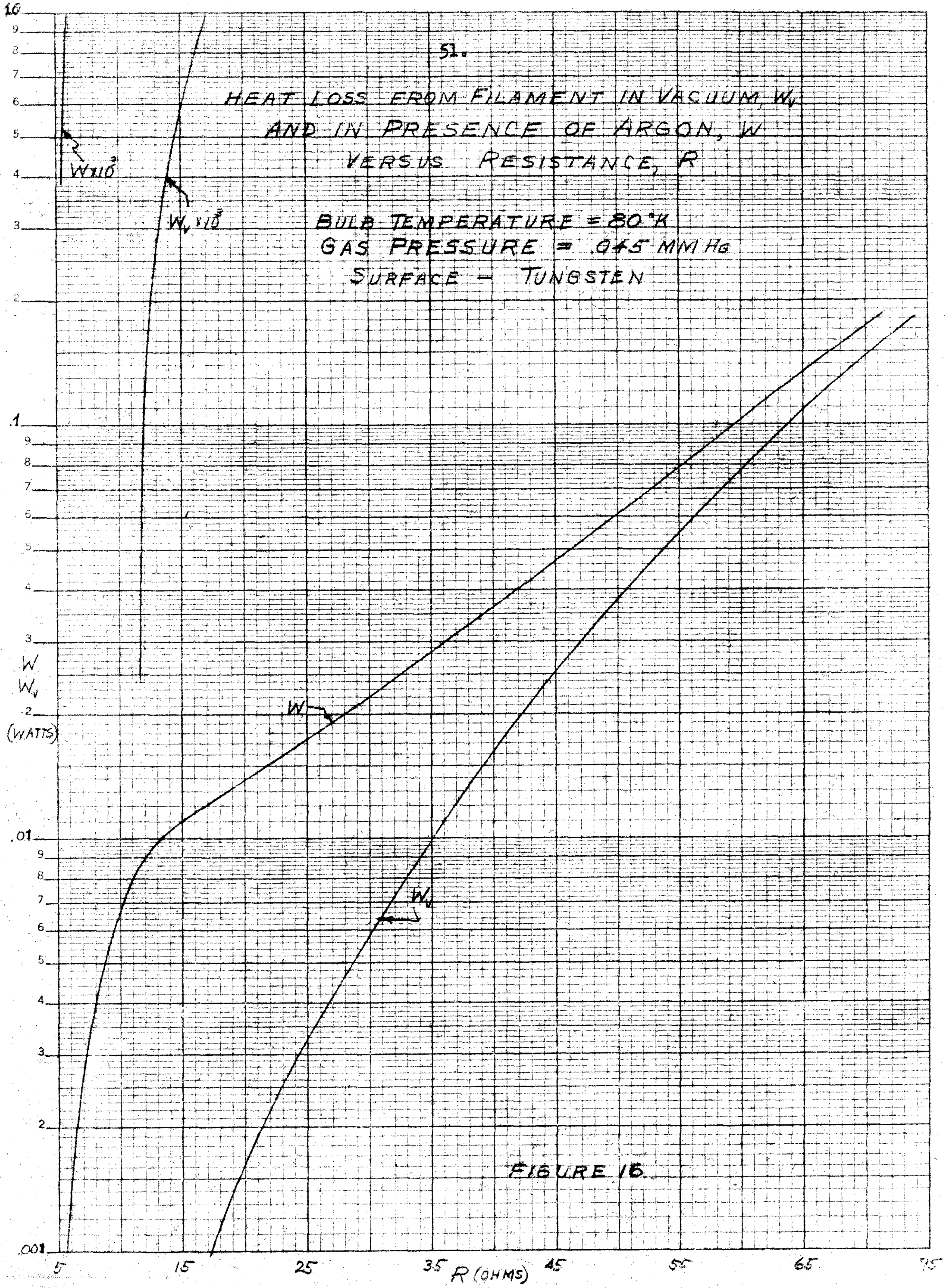
FIGURE 14



HEAT LOSS FROM FILAMENT IN VACUUM, W_v
AND IN PRESENCE OF HELIUM, W
VERSUS RESISTANCE, R

BULB TEMPERATURE = 80°K
GAS PRESSURE $p_1 = .034$ MM Hg
$p_2 = .150$ MM Hg
SURFACE — TUNGSTEN

FIGURE 15



HEAT LOSS FROM FILAMENT IN VACUUM, W_v
AND IN PRESENCE OF ARGON, W
VERSUS RESISTANCE, R

BULB TEMPERATURE = 80°K
GAS PRESSURE = .045 MM HG
SURFACE – TUNGSTEN

FIGURE 16

HEAT LOSS FROM FILAMENT IN VACUUM, W_v AND IN PRESENCE OF NITROGEN, W VERSUS RESISTANCE, R

BULB TEMPERATURE = 80°K
GAS PRESSURE = .037 MMHG
SURFACE — TUNGSTEN

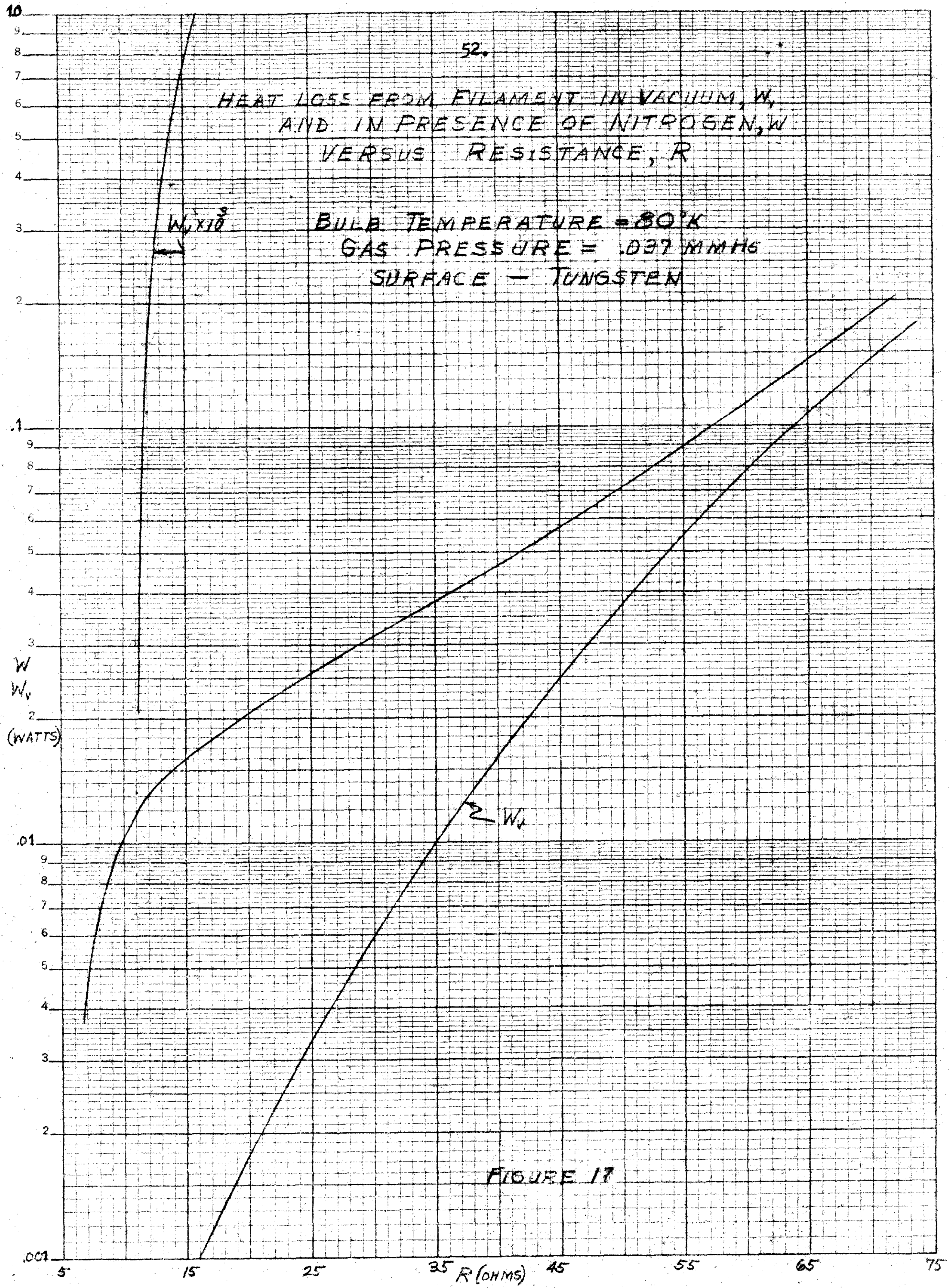


FIGURE 17

ACCOMMODATION COEFFICIENT VERSUS SQUARE ROOT OF GAS TEMPERATURE, T_b

FILAMENT TEMPERATURE = 855 °K

SURFACE - TUNGSTEN

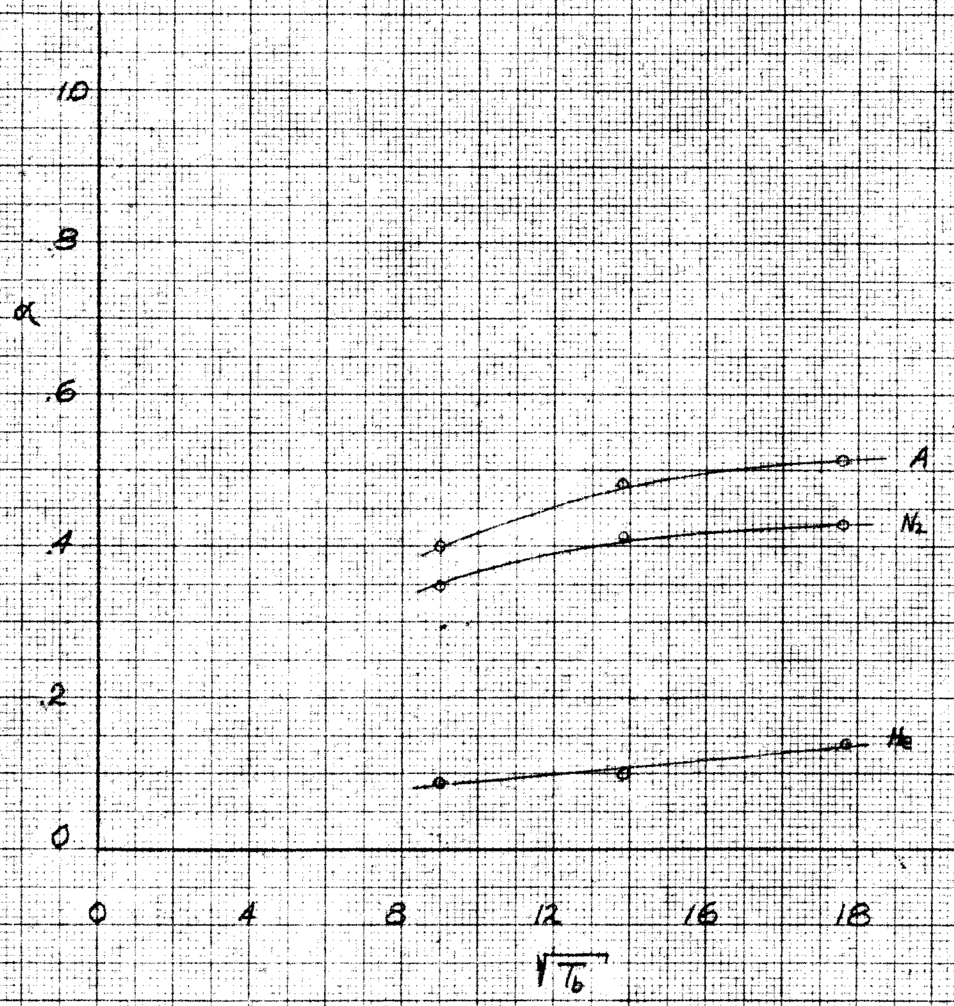


FIGURE 18

ACCOMMODATION COEFFICIENT VERSUS SQUARE ROOT OF GAS MOLECULAR WEIGHT

FILAMENT TEMPERATURE = 855°K
GAS TEMPERATURE = 300°K
SURFACE - TUNGSTEN

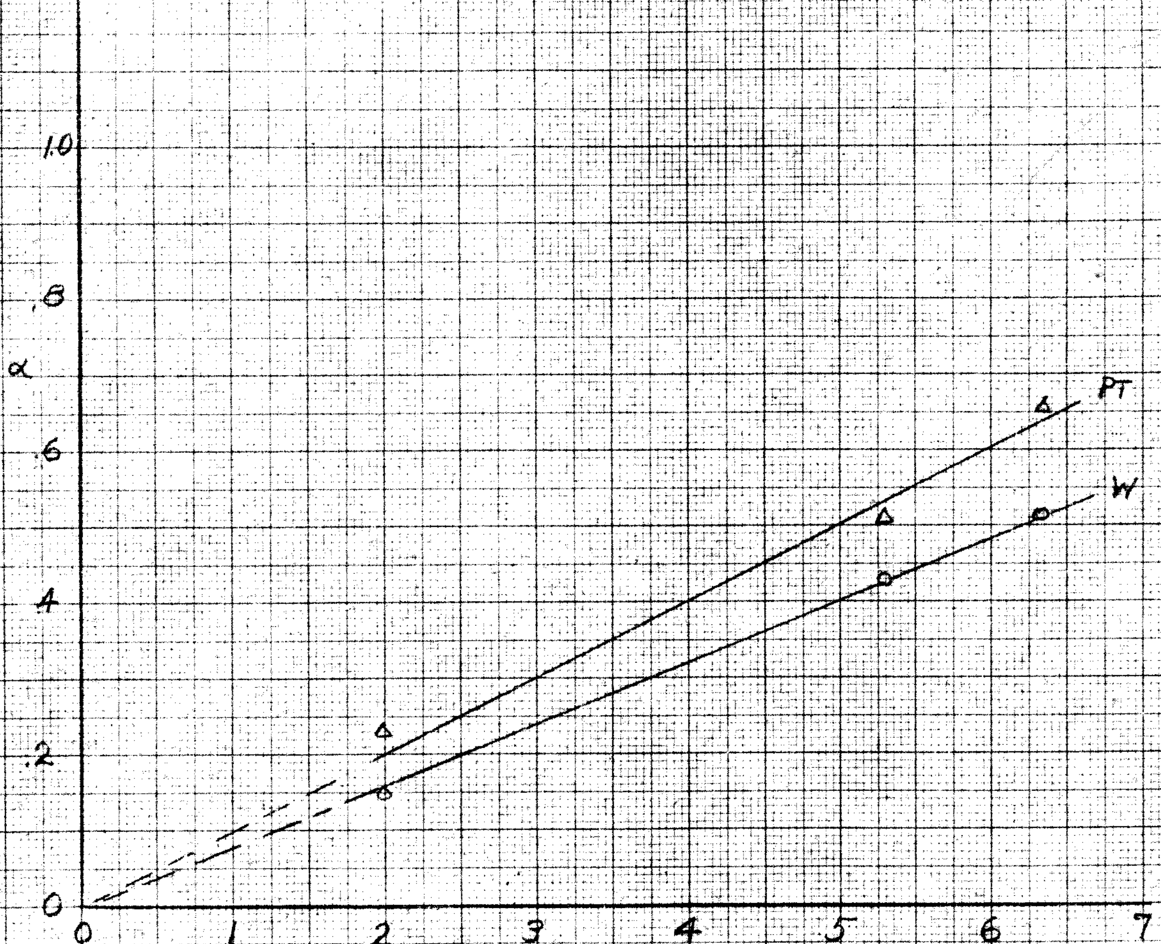
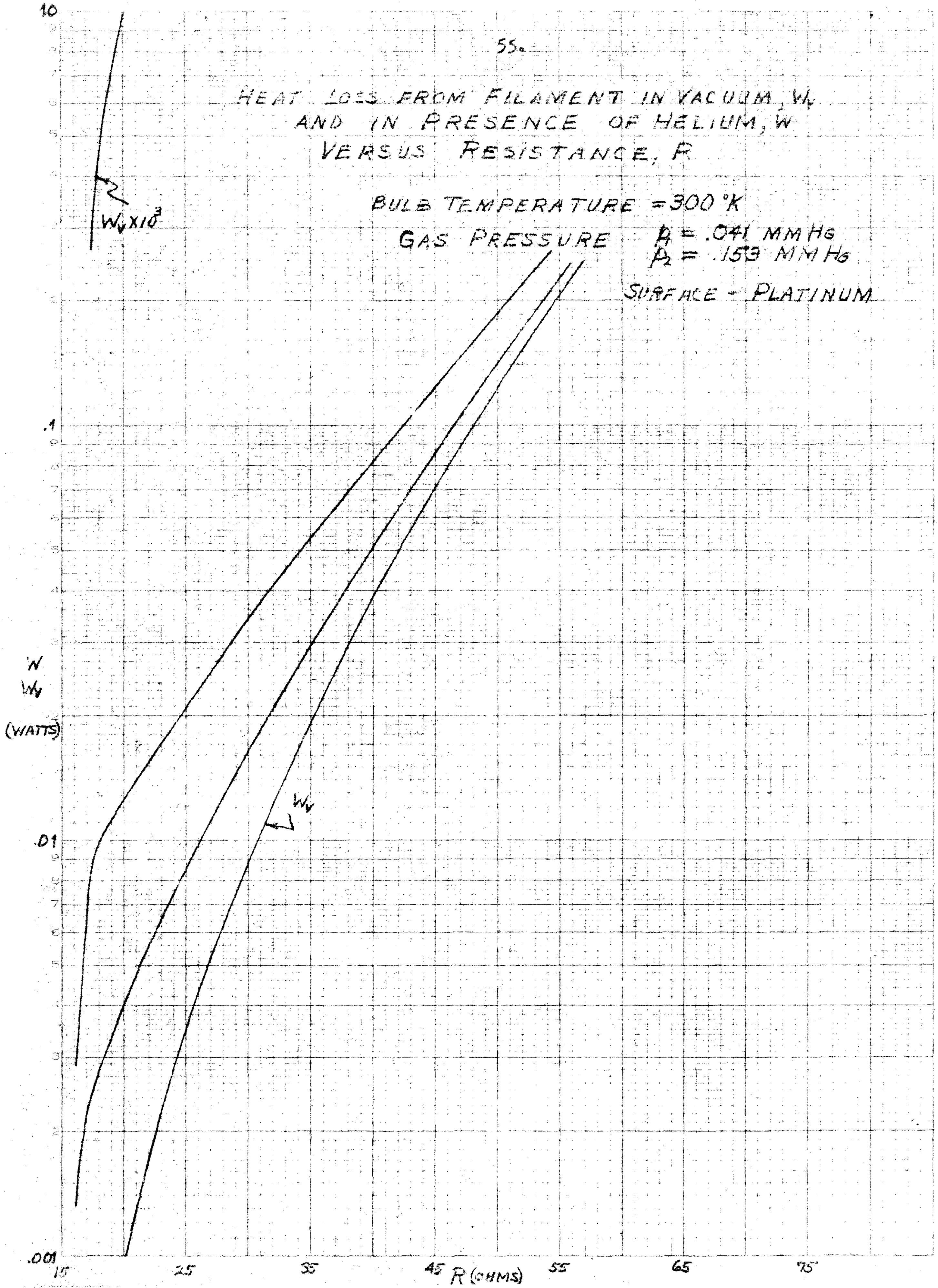
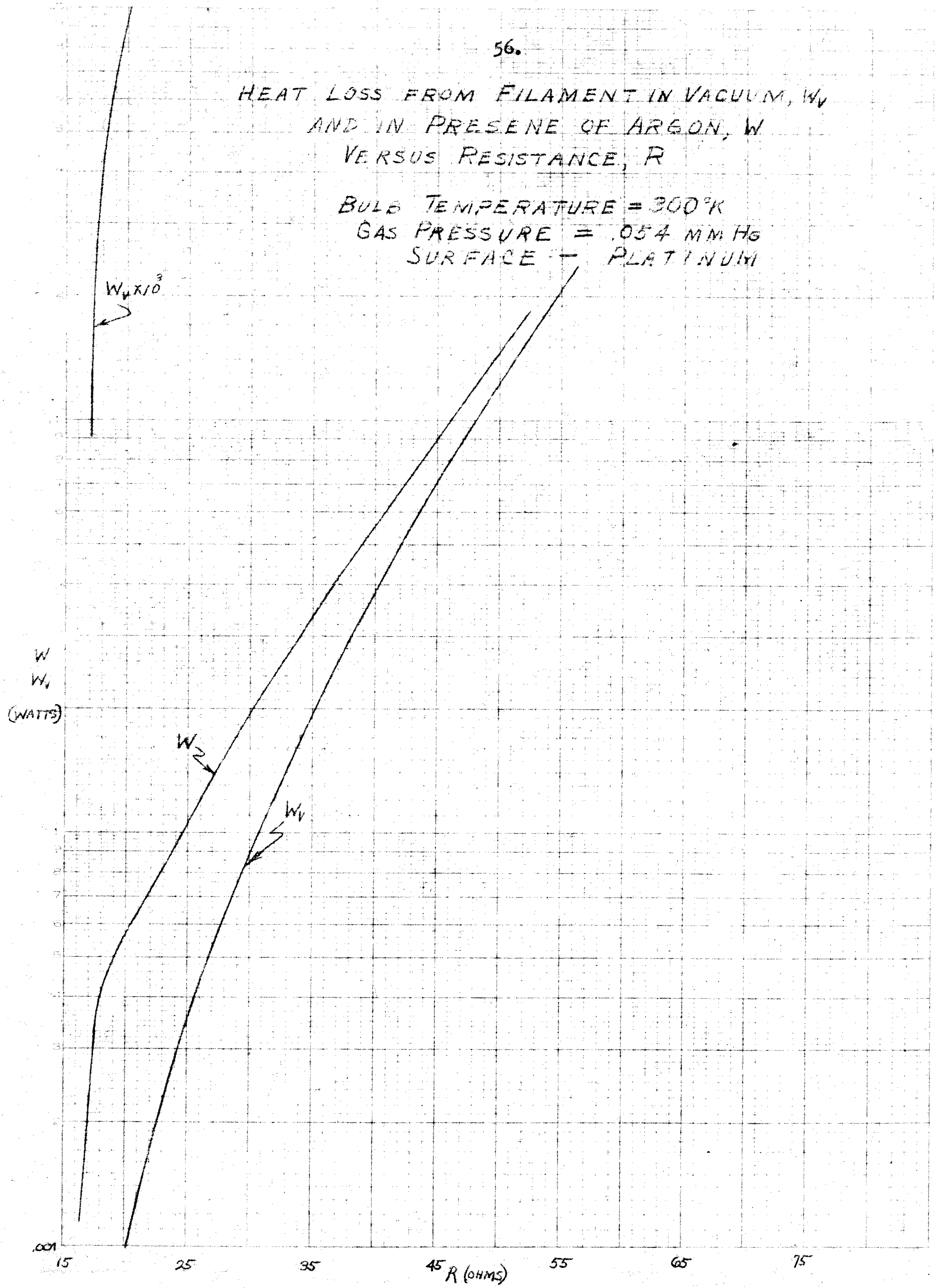


FIGURE 19

HEAT LOSS FROM FILAMENT IN VACUUM, W_v
AND IN PRESENCE OF HELIUM, W
VERSUS RESISTANCE, R

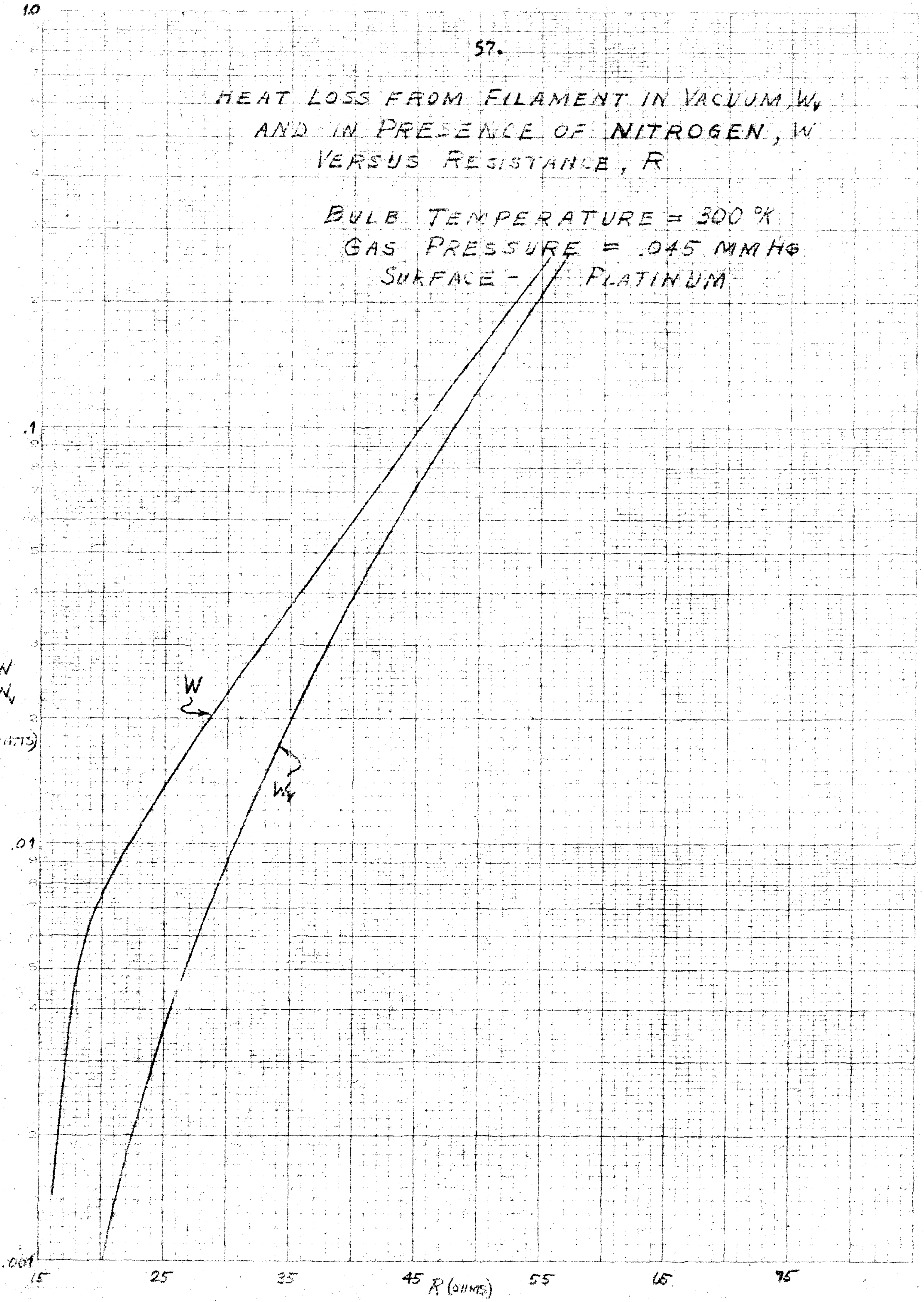
BULB TEMPERATURE = 300 °K
GAS PRESSURE p_1 = .041 MM HG
p_2 = .153 MM HG
SURFACE - PLATINUM





HEAT LOSS FROM FILAMENT IN VACUUM, W_V
AND IN PRESENE OF ARGON, W
VERSUS RESISTANCE, R

BULB TEMPERATURE = 300°K
GAS PRESSURE = .054 MM HG
SURFACE — PLATINUM



HEAT LOSS FROM FILAMENT IN VACUUM, W_v
AND IN PRESENCE OF NITROGEN, W
VERSUS RESISTANCE, R

BULB TEMPERATURE = 300 °K
GAS PRESSURE = .045 MM Hg
SURFACE - PLATINUM

RESISTIVITY, ρ, VERSUS TEMPERATURE, T FOR PLATINUM