I. EXPERIMENTAL DETERMINATION OF SELECTED ACCOMMODATION COEFFICIENTS

II. EXPERIMENTAL DETERMINATION OF THE HEAT OF DISSOCIATION OF IODINE

Thesis by

Raymond Louis Angelo
Lieut. Comdr., U.S. Navy

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ABSTRACT

In PART I the results of a study of the accommodation coefficient and its dependence on the temperature of the metal surface are described. The following systems were investigated: oxygen on platinum, carbon dioxide on platinum, nitrogen on platinum, carbon dioxide on tungsten, and carbon dioxide on nickel. All systems exhibit similar characteristics; i.e., a rapid rise to a maximum value of the accommodation coefficient in the region of low filament temperatures followed by a gradual decrease to a constant value as the filament temperature is increased, bulb temperature remaining constant.

	Maximum	Constant value
Oxygen-platinum	.98	.68
Nitrogen-platinum	.97	.50
CO_2 -platinum	.56	.35
CO_2 -tungsten	.93	.80
CO_2 - nickel	.68	.47

This general behavior of the accommodation coefficient substantiates findings reported earlier by Oliver (13) for other gas-metal systems.

The experimentally determined values of the accommodation coefficient are applied to a theoretical relation obtained by application of the theory of absolute reaction rates (10). The theoretical expression is shown to be in semiquantitative agreement

with the experimental data.

In PART II the "hot wire" method is used to determine the heat of dissociation of iodine. The experimentally determined value is 36.9 kcal/mole at 600°K. The presently accepted value for this temperature is 35.17 kcal/mole. Provided a wire can be found which is not corroded by fluorine, the present results suggest a useful method for determining the heat of dissociation of fluorine.

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PART I

EXPERIMENTAL DETERMINATION OF SELECTED ACCOMMODATION COEFFICIENTS

INTRODUCTION

The interchange of energy between a solid surface and a rarefied gas is a function of a parameter known as the accommodation coefficient. The initial conception of the accommodation coefficient is due to Knudsen (1), who defined it as representing the fractional extent to which those molecules that fall on the solid 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 Maxwellian stream at the temperature of the wall. As the equation for the accommodation coefficient Knudsen wrote

$$\alpha' = \frac{T_r - T_i}{T_w - T_i} \qquad (I - 1)$$

where T_i is the temperature of the incident molecules, T_r is the temperature of the reflected or re-emitted molecules, T_w is the surface temperature, and α' is the accommodation coefficient. In defining α' by Equation (I-1) Knudsen assumed that the reflected molecules leave the surface with a Maxwellian velocity distribution. Such a distribution can be expected only when the incident molecules reach thermal equilibrium with the surface before rebounding. This condition is nearly met when the temperature difference $T_w - T_i$ is small, but the departure from the Maxwellian distribution probably increases as the temperature difference increases. For theoretical and experimental purposes, Langmuir (2) and other later investigators found it convenient to write for the accommodation coefficient

$$\alpha = \frac{E_r - E_i}{E_w - E_i} \qquad \text{(I-2)}$$

where E_i and E_w represent the average energies of the gas at the initial and wire temperatures, respectively, and E_r is the average energy of the reflected stream of molecules. As defined by Equation (I-2) α has meaning for large values of $T_w - T_i$.

It is the purpose of this paper to present accommodation coefficient data for some systems for which measurements have not as yet appeared in the literature; namely, carbon dioxide on the metals platinum, tungsten, and nickel. In addition, nitrogen and oxygen on platinum are studied for a comparison with values already reported by other investigators.

LITERATURE SURVEY

Early experiments by Roberts (5) and Langmuir (6) showed not only that the accommodation coefficients of the gases helium and neon on a clean heated tungsten surface were extraordinarily low, but also that the values increased with time. Roberts suggested by way of explanation that there was a gradual formation of adsorbed films on the surface of the tungsten due to traces of impurities in the gas.

To learn more about the nature of these films, Mann (7) conducted a series of experiments on platinum wires under various conditions, platinum being relatively resistant to contamination. He reported values of α between .42 and .55 for filament temperatures between 100°C and 1000°C for the platinum-oxygen system. In the case of helium he found that α increased markedly with time from an initial low value of .066 obtained just after flashing the wire at an elevated temperature. He also observed that in subsequent experiments with the same filament the flashing time required to reproduce the initial low value for the coefficient was much less than the time required to remove the original film; i.e., the new films were less stable in nature. From his experments he concluded that the contamination of the wire was an adsorption process dependent not only on residual impurities in the gas, but also on the nature of the wire surface.

It is interesting to note that in the experiments with oxygen on platinum, Mann found that the oxygen "etched" the wire. This was evidenced by the loss in weight of the wire noticed upon the conclusion of the experiments. This loss in weight could have resulted from the boiling away of impurities in the platinum or of the platinum itself during prolonged heating at low pressures, however. No such phenomenon was noted in the present experiments. Though Mann did not make a specific study of the variation of the accommodation coefficient with temperature, he did make mention of an increase in the value with the lowering of temperature which "is immediate and does not seem to be due to contamination." This last statement is in accord with results obtained by the author.

In later experiments, Roberts (8) studied the adsorption of traces of gases mixed with neon by observing the resulting change in the accommodation coefficient of the neon-tungsten system. The accommodation coefficient for this particular system had been found to be unusually sensitive to the presence of adsorbed films on the metal. The partial pressure of the gas undergoing adsorption was determined and maintained constant. A sketch of Roberts' apparatus is shown in Figure 1. Neon was continuously circulated through the charcoal tubes C_1 and C_2, which were cooled in liquid air to remove adsorbable impurities. Initially the filament W was flashed above 2000°K to clean the surface. After cooling, a

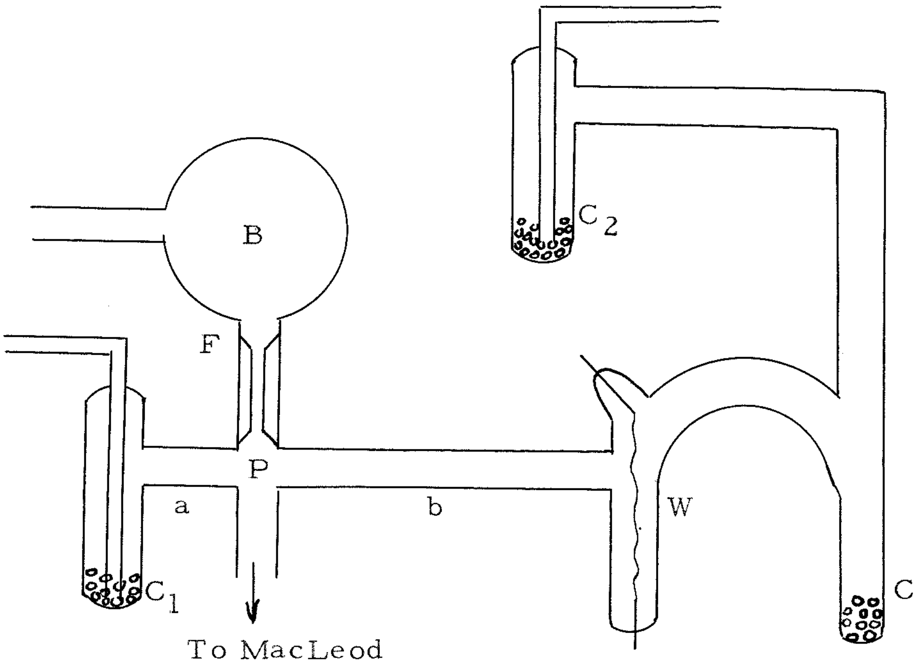

Figure 1

measured current was passed through the filament to raise its temperature about 20° above that of the oil bath in which the containing tube was immersed. Resistance-time readings were taken, from which the temperature of the wire could be found and the accommodation coefficient of neon determined. At a given instant, a measured amount of oxygen was admitted to the bulb B. The gas diffused through the capillary F and divided into three streams, One filled the MacLeod pressure gage, one went to C_1 where it was removed, and the third went past the wire to C, a small fraction of this stream going to C_2. The change in the accommodation coefficient was measured.

Roberts found that at room temperatures there is a film of oxygen which is stable at the lowest pressures. Above this film there is another, the population of which depends on the pressure. The mean life of a particle on the surface of this film is not less than about 2 seconds. The lower film is itself composite--part of it evaporating at about 1100°K and the rest not until above 1700°K.

In a quantum mechanical treatment Devonshire (9) attempted to take into account the attractive field known to exist between the solid and gas by supposing that the interaction potentials between the solid and gas could be represented by a Morse potential function. In developing his theoretical expression for the accommodation coefficient, he assumed (a) all gas atoms move perpendicularly to the solid surface and (b) the solid is composed of harmonic oscillators which only take up or give up one quantum of energy at a time. He arrived at the expression

$$\alpha = \frac{E_r - E_i}{E_w - E_i} = \frac{h}{k^3 T_w^3} \int_0^{\nu_m} (h\nu)^2 d\nu \int_0^{\infty} G(E, E+h\nu)\, e^{-E/kT_w}\, dE \qquad \text{(I-3)}$$

where $E_w - E_i = k(T_w - T_i)$, i.e. $T_w - T_i$ is small, and $G(E, E+h\nu)d(h\nu)$ is the probability that the atom will take up a quantum of energy from the solid in the frequency range $(\nu, \nu + d\nu)$. Satisfactory agreement with experimental values obtained by Roberts for helium and neon on tungsten was noted, permitting an estimate of the value of the constants of the potential field. Devonshire pointed out that the theory was valid only for a surface free from adsorbed gases and hence probably would not be applicable at very low temperatures when there might be several adsorbed layers. A theoretical relation for the accommodation coefficient has been obtained by Wise and Altman (10) who used the theory of absolute reaction rates (Cf. Reference 11) together with simplifying assumptions concerning the nature of molecules adsorbed on a metal surface. The accommodation coefficient may be interpreted to represent either (a) an average in which all the gas falling on the surface receives a fraction of the energy necessary to bring the gas to thermal equilibrium with the surface or (b) the fraction of the incident molecules which adhere to the solid and become desorbed from the solid at the surface temperature with a Maxwellian velocity distribution. Wise and Altman use this latter interpretation to obtain the following expression for the accommodation coefficient of a monatomic gas:

$$\alpha = c_s \cdot \frac{h^2}{2\pi m k (T_i)^{-1/2} (T_w)^{3/2}} \cdot e^{-\epsilon_a/kT_w} \qquad \text{(I-4)}$$

Here c_s is the total number of surface sites on which atoms may become adsorbed per unit area, ϵ_a is the energy of activation for adsorption, h is the Planck constant, and k is the Boltzmann constant. For a constant T_i the analysis shows a maximum value of α as T_w approaches the value $\epsilon_a/3$. Thus from experimental measurements of α as a function of surface temperature T_w holding gas temperature T_i constant, ϵ_a may be estimated. Although the equation appears to have the correct functional form in so far as the dependence of α on T_w is concerned, the result contains adjustable parameters (e.g., the activation energy for adsorption) which must at present be determined experimentally.

In an effort to account in some measure for the wide variation in reported values for the accommodation coefficient of a given gas-metal system, Thomas and Brown (3) measured values of the coefficients of nine gases on platinum as functions of temperature and pressure. Six different types of tubes were used in order to duplicate apparatus used by previous investigators. Thomas and Brown found that in all cases, contrary to results published by Amdur (4), the accommodation coefficients showed a constant value as the pressure was lowered toward zero and a decrease in value as the pressure was raised above 20 microns of mercury. They attributed the divergence in reported values to the variety of methods and vacuum techniques used by different experimenters, and to the possible presence of impurities in the vacuum systems or in the gases being studied. It was thought that these impurities formed adsorbed layers on the metal surface, resulting in the measurement of an excessively large value for α.

THEORY

The accommodation coefficient, α, as used in this paper is defined by the relation

$$\alpha = \frac{E_r - E_i}{E_w - E_i} \tag{I-2}$$

where E_i is the energy carried by the incident stream to unit area of the wire per second, E_r is the energy carried away from unit area of the wire per second by the reflected stream, and E_w is the energy which would be carried away from unit area of the wire surface per unit time by a stream at the temperature of the wire.

Kennard (12) gives for the heat conduction process to a plate at temperature T_2 from a parallel plate at temperature T_1 the relation

$$E_1' - E_2' = \alpha_2 (E_1' - E_2) \tag{I-5}$$

where E_1' and E_2' are the energies of the gas streams leaving plates 1 and 2, respectively, and α_2 is the accommodation coefficient for the gas on the second plate. If the heat conduction between two concentric cylinders of radii r_1 and r_2 $(r_2 \quad r_1)$ at temperature T_1 and T_2 respectively, is considered, it is possible to write (12)

$$E_1' \frac{r_1}{r_2} + E_2'\left(1 - \frac{r_1}{r_2}\right) - E_2' = \alpha_2 \left[E_1' \frac{r_1}{r_2} + E_2'\left(1 - \frac{r_1}{r_2}\right) - E_2\right] \tag{I-6}$$

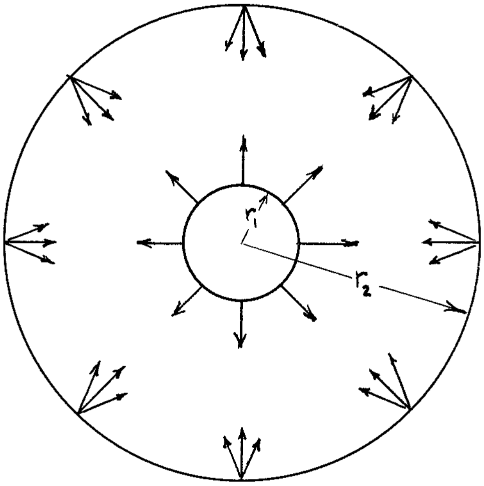

Figure 2

Here E_1' is the energy per unit area per second which is reflected from the inner cylinder, E_2' is the energy per unit area per second reflected from the outer cylinder, and α_2 is the accommodation coefficient between the gas and outer cylinder. E_2 is the energy per unit area per second of a stream issuing from a gas at temperature T_2. The total energy incident on the outer cylinder is carried by the molecules which leave the inner cylinder and the molecules which come from the outer cylinder itself (Cf. Figure 2). It is seen that all molecules which rebound from the inner cylinder must strike the outer one. Since the areas of the two cylinders are in the ratio r_1/r_2, the energy brought to unit area of the outer cylinder from unit area of the inner cylinder will be reduced by this ratio. The contribution to the total incident energy brought to the outer cylinder by those molecules which arrive from other portions of the outer cylinder is clearly $E_2'(1 - r_1/r_2)$, since $E_2' \, r_1/r_2$ represents the energy which is intercepted by the inner cylinder. Hence the total energy incident on the outer cylinder per unit area per second becomes $E_1' \, r_1/r_2 + E_2'(1 - r_1/r_2)$ and the heat conduction equation takes the form shown above (Equation I-6). Rearranging,

$$E_1' - E_2' = \frac{\alpha_2}{\frac{r_1}{r_2} - \alpha_2 \frac{r_1}{r_2} + \alpha_2} (E_1' - E_2) \tag{I-7}$$

Comparing with the equation given for parallel plates at temperatures T_1 and T_2, it is seen that the accommodation coefficient between the gas and outer cylinder is modified by the factor $\frac{1}{r_1/r_2 - \alpha_2 r_1/r_2 + \alpha_2}$. As r_2/r_1 is increased, however, this factor approaches $1/\alpha_2$ and E_2' becomes equal to E_2. For the experimental arrangement used in the present studies r_1/r_2 is sufficiently small to justify the assumption that $E_2' = E_2$.

For the energy incident on the inner of the two cylinders, clearly

$$E_2' - E_1' = \alpha_1 (E_2' - E_1) \tag{I-8}$$

where α_1 is the accommodation coefficient for the gas and inner cylinder. As this is exactly the equation for the energy transfer between parallel plates, no multiplicative factor is necessary in extending the parallel-plate results to the inner of two concentric cylinders.

In the problem under investigation the inner concentric cylinder is a fine metal wire at temperature T_w and the outer cylinder is a cylindrical glass bulb at temperature T_b. The accommodation coefficient is thus given by

$$\alpha = \frac{E_r - E_b}{E_w - E_b} \tag{I-9}$$

The translational energy carried by a stream issuing from a gas at temperature T_b is $2RT_b$ ergs per gram, R being the gas constant per gram. This is 4/3 times as great as the mean translatory energy of a gram of gas in equilibrium at the same temperature, the difference being due to the fact that the faster molecules both issue in larger numbers and carry more energy (12). The total energy brought up by one gram of such a stream is then

$$2RT_b + U_{ib}$$

where U_{ib} is the internal energy of the molecules in a gram at temperature T_b. Similarly, a stream at temperature T_w would transport

$$2RT_w + U_{iw}$$

units of energy. The energy difference, $E_w - E_b = \Delta E$, per gram is thus

$$\begin{aligned} \Delta E &= (2RT_w + U_{iw}) - (2RT_b + U_{ib}) \\ &= 2R(T_w - T_b) + \int_{T_b}^{T_w} \frac{dU_i}{dT}\, dT \end{aligned}$$

Since $C_v = \frac{3}{2}R + \frac{dU_i}{dT}$ (Cf. Ref 12)

$$\Delta E = 2R(T_w - T_b) + \int_{T_b}^{T_w} (C_v - \tfrac{3}{2}R)\,dT$$

$$\Delta E = \tfrac{1}{2}R(T_w - T_b) + \int_{T_b}^{T_w} C_v\,dT$$

or per molecule,

$$\begin{aligned}\Delta E &= \frac{mR}{2}(T_w - T_b) + m\int_{T_b}^{T_w} C_v\,dT \\ &= \frac{k}{2}(T_w - T_b) + k\int_{T_b}^{T_w} \beta\,dT \\ &= k\left(\frac{T_w - T_b}{2} + \int_{T_b}^{T_w} \beta\,dT\right) \\ &= k\int_{T_b}^{T_w} (\beta + \tfrac{1}{2})\,dT\end{aligned} \qquad \text{(I-11)}$$

where m = mass of molecule in grams

k = Boltzmann constant

β k = specific heat per molecule.

From kinetic theory, the number of molecules crossing unit area per second in a Maxwellian stream is given by

$$\nu = \frac{p}{(2\pi m k T)^{1/2}} \qquad \text{(I-12)}$$

Applying these results to a wire at temperature T_w and an incident stream of molecules at temperature T_b which reach thermal equilibrium with the wire and rebound at temperature T_w, the energy loss per unit area per second is

$$\Delta E = \frac{p}{(2\pi m k T_b)^{1/2}} \cdot k\int_{T_b}^{T_w} (\beta + \tfrac{1}{2})\,dT \qquad \text{(I-13)}$$

Thus the total power loss from the wire is

$$W_T = \pi \ell d \Delta E \tag{I-14}$$

where W_T represents the power loss which would accrue if all incident molecules reached the temperature T_w before rebounding. The accommodation coefficient for this case would be unity. In accord with our earlier remarks, we define the accommodation coefficient by the relation

$$\alpha = \frac{W_o}{W_T} \tag{I-15}$$

where W_o is the observed power loss.

Hence,

$$\alpha = \frac{W_o (2\pi m k T_b)^{1/2}}{\pi d \ell p k \int_{T_b}^{T_w} (\beta + \frac{1}{2}) dT} \tag{I-16}$$

where the following set of consistent units may be used:

W_o in ergs/sec

m in grams

k in ergs/°K/molecule

ℓ, d in cm.

p in dynes/cm^2

β k in ergs/°K/molecule

DESCRIPTION OF APPARATUS

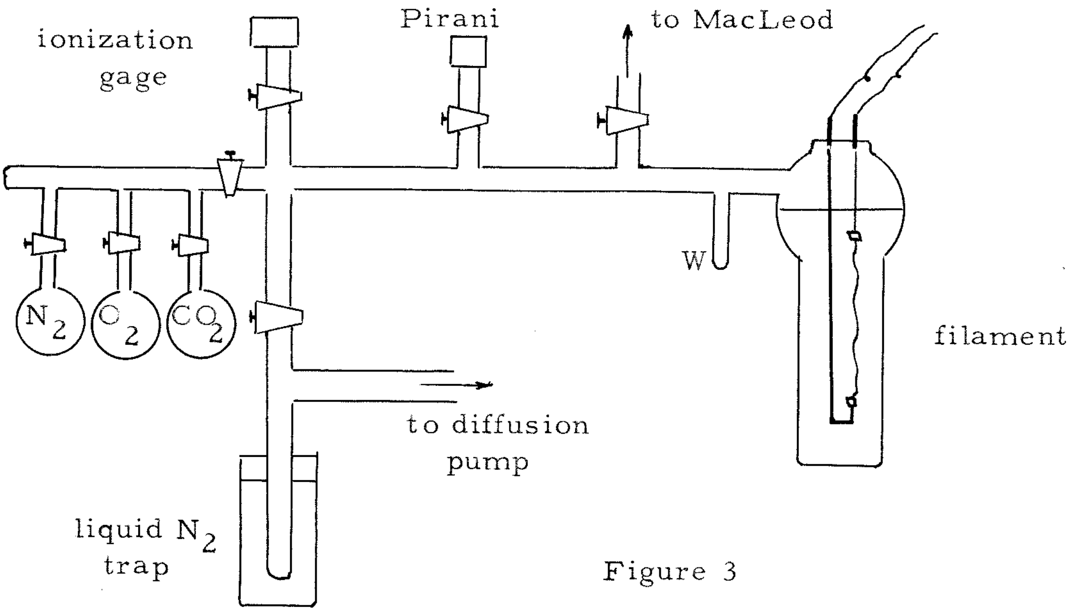

Figure 3

Pressure System

A schematic diagram of the equipment used in the experiments on both the accommodation coefficient and the heat of dissociation of iodine is shown in Figure 3. The apparatus is essentially the same as that used by Farber and Oliver (13). A triple-stage oil diffusion pump evacuated the system to a pressure of approximately 10^{-7} millimeters of mercury, as indicated by an ionization pressure gage.

The flasks containing the gases used during the accommodation coefficient experiments were fused directly into the system to minimize contamination due to connection leaks or dirty tubing.

For convenience, a Pirani gage was added to the system to provide an instantaneous indication of the pressure of a gas admitted to the bulb. At the low pressures required for the experiments, however, the Pirani gage readings were not sufficiently accurate to be used for calculating the accommodation coefficient. Accurate indications of pressure for this purpose were obtained from a MacLeod type gage, which has the advantage that it does not require recalibration for each experiment as does the Pirani gage.

The glass bulb containing the filament was 4 inches in diameter and 10 inches in length. The filament consisted of a single strand of wire suspended vertically between a pair of metal blocks attached to a thin metal rod inside the bulb. To insure good electrical contact the filament ends were clamped between pieces of thin gold plate in the blocks. The filament length of 4-1/2 inches varied somewhat from one experiment to another.

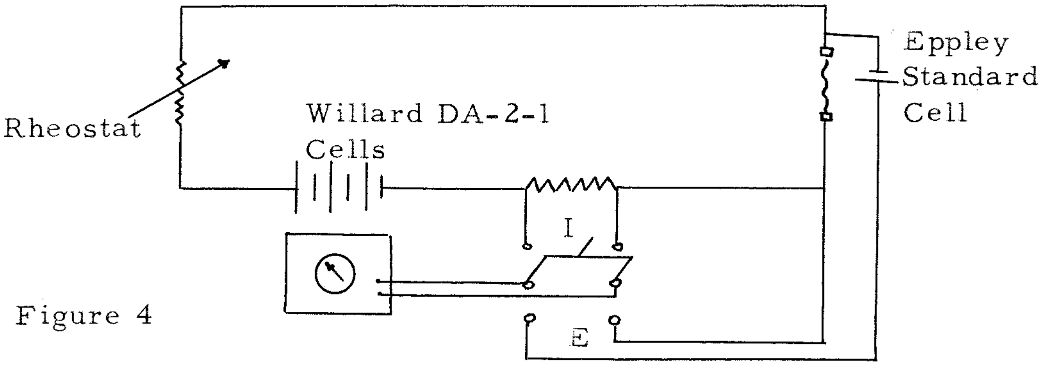

Figure 4

Electrical System

As indicated in Figure 4, power was supplied to the filament by Willard DA-2-1 storage cells. This type of cell was chosen for its ability to give constant voltage under low amperage operating conditions.

The voltage drop across a precision 3-ohm resistor in the filament circuit was used to determine the filament current. This voltage drop and the voltage drop across the filament itself were measured with a Rubicon precision potentiometer which allowed voltage measurements up to 1.61 volts. When the filament voltage exceeded this value, one or more calibrated Eppley Standard Cells were placed in series with the potentiometer to oppose the filament voltage and permit measurement.

A rheostat in the filament circuit provided a means of varying the power supplied to the filament. It was possible to measure filament power and resistance to an accuracy of 0.5 per cent.

Filaments and Gases

Pure tungsten and platinum filaments were obtained from the Sigmund Cohn Company of New York. The diameters of the tungsten and platinum wires were .001 and .00125 inches respectively. The gases oxygen and nitrogen were obtained from the

Air Reduction Company in one-liter flasks. The nitrogen contained no impurities detectable by mass spectrometer, while the oxygen contained .4% argon and .1% nitrogen. The carbon dioxide was of commercial quality and was redistilled in the laboratory prior to use in the experiments.

EXPERIMENTAL METHOD

It is evident that the accommodation coefficient has meaning only for a clean surface; i.e., one that is free from any adsorbed gas layers. The rate of adsorption of gas molecules on a metal surface is known to increase with pressure and decrease with temperature of the surface; therefore the experiments were conducted using bulb pressures as low as practicable, the lower limit being determined by the necessity for a power loss from the filament to the gas large enough for accurate measurement. It was also desirable to operate at pressures low enough so that the mean free molecular path was large in comparison with the bulb diameter. In so doing, it is unnecessary to take into account exchange of energy between the gas molecules themselves; the temperature of the impinging molecules is the bulb temperature. This condition is necessary to validate the assumption that the accommodation coefficient is independent of pressure in the range of pressures used in the experiments. It is interesting to note here that Langmuir (14), in measuring the accommodation coefficient of the hydrogen-tungsten system at somewhat higher pressures, corrected for thermal conduction through the gas by assuming the temperature of the molecules impinging on the filament to be the temperature of molecules one mean free path length away from the filament. This temperature was calculated from the ordinary laws of heat conduction through a gas.

The conditions imposed on the pressure, as outlined above, were found to be satisfied in the range of pressures from 20 to 50 microns of mercury.

To remove any initial adsorbed gas layers from the filaments, the bulb was evacuated to a pressure of approximately 10^{-7} millimeters of mercury and the filament "flashed" at a suitable temperature (1400°K for platinum, 2000°K for tungsten). Bremner (15), in a recent paper, attaches much importance to the flashing technique and attributes the wide divergence in the reported values of the accommodation coefficient to the varying flashing procedures used by the different investigators. It should be pointed out that Bremner used the Knudsen definition of the accommodation coefficient (Cf. Equation I-1) which imposes the condition that the difference between the temperatures of the incident molecules and of the surface be small. If, after being flashed at an elevated temperature, a filament is cooled down to within a few degrees of the bulb temperature (assuming the bulb to be at room temperature or nearly so), it is reasonable to expect that adsorbed gas layers will begin to form on the filament, and that the value of the accommodation coefficient will show an increase with time. Thus the time elapsing between flashing and making measurements and the length of the flashing period become of importance.

At the start of the present experiments it was decided to investigate the effect of varying the flashing time on the power loss versus filament temperature relationship, both in vacuo and in the gas. Reproducible results were obtained for flashing times of five minutes, twenty minutes, and forty minutes; hence it was decided that a flashing period of at least five minutes would be sufficient for all succeeding experiments. Increasing the flashing temperature 100°K produced no noticeable effect. Care must be taken not to flash at a temperature too near the melting point of the metal. It is likewise important to consider the fact that the filament metal may evaporate appreciably at the higher filament temperatures. The steps in the experimental procedure are outlined below:

(a) The filament was fastened into position in the bulb and the bulb evacuated to a pressure of approximately 10^{-7} millimeters of mercury. During the evacuation, the walls of the bulb and the connecting tubing were flamed with a Bunsen burner to drive off any adsorbed gases on these surfaces.

(b) The filament was flashed for at least five minutes at the appropriate temperature to clean the surface.

(c) Filament current and voltage drop readings were made over the range of temperatures from room temperature (298°K) to about 1400°K.

(d) Gas was admitted until the system pressure was approximately 30 microns of mercury. After a second five-minute flashing period, filament current and voltages were recorded over the same temperature range.

(e) The bulb was immersed in a temperature-controlled bath, and the current and voltage measurements were repeated.

CALCULATION OF THE ACCOMMODATION COEFFICIENT

The expression for the accommodation coefficient as previously derived is

$$\alpha = \frac{W_o}{W_T} = \frac{W_o\,(2\pi m k T_b)^{1/2}}{k p \pi \ell d \int_{T_b}^{T_w} (\beta + \frac{1}{2})\, dT} \qquad \text{(I-16)}$$

where W_o = observed energy loss, ergs/sec

m = mass of molecule, grams

p = pressure, dynes/cm^2

d = filament diameter, cm.

ℓ = filament length, cm.

k = Boltzmann constant, ergs/^{o}K

βk = specific heat at constant volume per molecule, ergs/^{o}K

T_b = bulb temperature, ^{o}K.

T_w = filament temperature, ^{o}K.

Substitution of the appropriate molecular masses and conversion factors leads to

$$\alpha_{O_2} = .578\ \frac{W_o T_b^{1/2}}{\ell d p \int_{T_b}^{T_w} (\beta + \frac{1}{2})\, dT}$$

$$\alpha_{N_2} = .538\ \frac{W_o T_b^{1/2}}{\ell d p \int_{T_b}^{T_w} (\beta + \frac{1}{2})\, dT}$$

$$\alpha_{CO_2} = .680\ \frac{W_o T_b^{1/2}}{\ell d p \int_{T_b}^{T_w} (\beta + \frac{1}{2})\, dT}$$

where now W_o = observed power loss, watts

p = pressure, millimeters of mercury

d = filament diameter, inches

ℓ = filament length, inches

Values of β as a function of temperature for the various gases are readily available (Cf. Reference 16). For the determination of W_o, curves of filament power loss versus filament temperature in vacuo and in the gas are plotted on the same graph. The vacuum curve represents the radiated power loss, hence W_o is obtained by taking the difference between the two curves at the same temperature. Filament current and voltage drop readings provide a measure of the power loss and filament resistance. From the resistance and known dimensions of the filament, the resistivity is found. The filament temperature can then be determined from curves of resistivity versus temperature for the filament material.

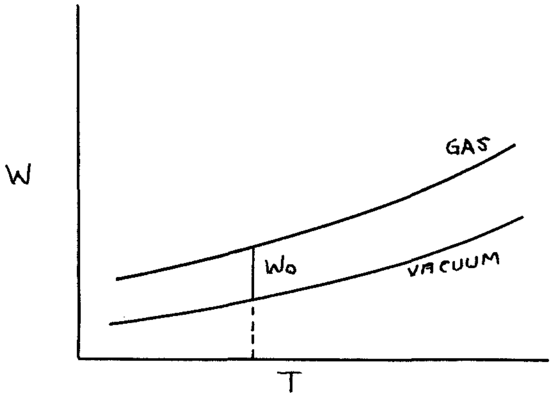

Figure 5

The ends of the filament, where they are attached to the larger, cooler electrical leads, remain at a temperature considerably lower than the body of the filament and hence lower the overall resistance of the filament. The measured filament resistance thus corresponds to some average temperature which is lower than the true temperature. Langmuir and Dushman (17) developed an empirical relation to correct for this end cooling effect in the form of a correction factor, f.

$$f = \frac{V + 2\Delta V}{V} \tag{I-17}$$

where V is the observed voltage drop and ΔV is the voltage drop lowering due to cooling at the end of one lead. ΔV is given by the equation

$$\Delta V = 1.394 \times 10^{-5} T^{1.3} - 4.894 \times 10^{-3} T^{.3} \text{ for } T \leq 1200^{\circ}\text{K} \tag{I-18a}$$

and $$\Delta V = 0.9897 \times 10^{-5} T^{1.3} \text{ for } T > 1200^{\circ}\text{K} \tag{I-18b}$$

INTERPRETATION OF RESULTS

Curves of the accommodation coefficient as a function of temperature for the systems nitrogen-platinum, oxygen-platinum, carbon dioxide-platinum, carbon dioxide-nickel, and carbon dioxide-tungsten are shown in Figures 9 through 13. Representative values for comparison are given in tabular form below:

Gas	Filament	T_{bulb}	T_{wire}	$T_w - T_b$	a
Nitrogen	Platinum	298°K	1000°K	702°	.50
Oxygen	Platinum	298°K 208°K 77°K 341°K	1000°K 910°K 779°K 1043°K	702° 702° 702° 702°	.66 .61 .47 .78
CO_2	Platinum	298°K 347°K	1000°K 1049°K	702° 702°	.35 .37
CO_2	Nickel	298°K	1000°K	702°	.47
CO_2	Tungsten	298°K	1000°K	702°	.80

TABLE I.

All curves exhibit the same general characteristics, i.e., an initial rapid rise to a maximum value followed by a gradual decrease to a final constant value. In all cases the maximum occurs in the region where $T_w - T_b$ is small, which immediately suggests that at the lower temperatures (a) a film of the gas molecules forms on the filament, and (b) the heat of desorption of gas molecules from the wire surface constitutes a considerable portion of the total heat loss. Either factor would tend to increase the apparent value of the accommodation coefficient. The curves of accommodation coefficient versus temperature difference $T_w - T_b$ likewise show that the accommodation coefficient is not independent of gas temperature. For a given temperature difference, the accommodation coefficient increases roughly as the square root of the gas temperature as shown in Figure 15.

For oxygen on platinum Thomas and Brown (3) obtained a value of .68 with a temperature difference of 167°C, the bulb being at room temperature (298°K). Reference to Figure 10 shows the value .85 for this same temperature difference and bulb temperature. There is better agreement at a temperature difference of 22°C, however. Thomas and Brown reported the value .70, while the value .70 was also obtained in the present experiments. It should be noted that in both instances the values compared lie in the temperature region of rapidly changing α, and hence lie in a region where small errors in T_w will greatly influence the results.

Values of α obtained at low filament temperatures are especially questionable when the bulb is immersed in a cold bath. Unless the filament leads can be brought to and maintained at the bulb temperature, heat will flow into the filament from the warmer surroundings with the result that the power required to heat the filament to a given temperature will be less than that normally needed. The design of the apparatus used in the present experiments was such that it was impossible to maintain the filament leads at the bulb temperature when the bulb was immersed in the cold baths. The theoretical analysis developed by Wise and Altman (10) was applied to the experimentally observed results, which were used to determine the activation energy for adsorption. A comparison between the experimental data and theory is not strictly applicable because the Wise-Altman equation (I-4) was developed for monatomic gases and does not include the vibrational-rotational contributions of a diatomic molecule to the partition functions. However, in the range of temperatures used in the present experiments (T_w less than 1500°K) the contributions to the partition function are probably small enough to be neglected. The Wise-Altman theoretical expression for the accommodation coefficient is

$$\alpha = C_s \frac{h^2}{2\pi m k} \frac{T_b^{1/2}}{T_w^{3/2}} e^{-\epsilon_a/kT_w} \qquad (I-4)$$

Holding T_b constant and assuming c_s to be independent of filament temperature, we have

$$\alpha = \text{constant} \cdot \frac{1}{T_w^{3/2}} \cdot e^{-\epsilon_a/kT_w}$$

$$\text{or,} \quad \frac{d \ln \alpha}{d T_w} = -\frac{3}{2}\frac{1}{T_w} + \frac{\epsilon_a}{k T_w^2}$$

When the value of α is a maximum, $\frac{d \ln \alpha}{d T_w} = 0$

$$\therefore \epsilon_a = \frac{3}{2} k T_w \Big|_{\alpha_{max}}$$

$$= 2.072 \times 10^{-16} T_w \Big|_{\alpha_{max}} \text{ ergs/molecule}$$

$$= 2.983 \; T_w \Big|_{\alpha_{max}} \text{ cals/mole}$$

For two of the systems investigated, the results of the above calculation are shown in Table 2.

System	$T_{w_{\alpha max}}$	cals/mole
Nitrogen-platinum	340	1015
Oxygen-platinum	380	1135

TABLE 2

The number of active surface sites on the metal surface, c_s, can be estimated by substitution of the ϵ_a calculated values into Equation (I-4). The value of α used in the equation is taken from the experimental curves at the given T_b and T_w. The results of two such calculations are shown in Table 3.

Gas	Metal	c_s sites/cm^2
0_2	Platinum	21.1×10^{17}
N_2	Platinum	16.23×10^{17}

TABLE 3

Equation (I-4) predicts that for any given metal surface, α is proportional to the square root of the gas temperature for constant filament temperature. In Figure 14, α versus $\sqrt{T_b}$ for the oxygen-platinum system is plotted at a filament temperature of 1000°K.

In Table 4 experimental values of the accommodation coefficient of oxygen on platinum are compared with values calculated from Equation (I-4). In making these computations, the experimentally determined values, ϵ_a = 1135 cals/mole and c_s = 21.1×10^7 sites/cm^2 at T_b = 298°K. were used. These data are plotted in Figure 16a.

T_w (°K)	(theoretical)	(experimental)
300	.880	.706
400	.915	.946
500	.875	.820
600	.791	.735
700	.724	.706
800	.655	.679
900	.593	.679
1000	.540	.679
1100	.490	.679
1200	.450	.679

TABLE 4

The number of active surface sites for the nitrogen-platinum system, computed from the experimental data, is $16.23\text{x}10^{17}$. Using this value, and ϵ_a = 1015, Equation (I-4) was used to calculate the theoretical accommodation coefficient curve for this system. Data are tabulated in Table 5 and plotted in Figure 16b.

T_w (^{o}K)	(theoretical)	experimental)
300	.940	--
400	.935	.930
500	.870	.780
600	.772	.700
500	.698	.655
400	.624	.605
900	.561	.540
1000	.507	.500
1100	.455	.500
1200	.417	.500

TABLE 5

The good agreement between the theoretical and experimental curves is not too surprising when it is remembered that the constants used in the theoretical expression for the accommodation coefficient were derived from the experimental data. However, it can be seen that Equation (I-4) has the correct functional form.

PART II

EXPERIMENTAL DETERMINATION OF THE HEAT OF DISSOCIATION OF IODINE

INTRODUCTION

The heat of dissociation of a diatomic gas is defined by the chemist as the heat required to dissociate a gram molecule of the gas at standard temperature (usually 291°K) to monatomic gas at the same temperature. The spectroscopist finds it more convenient to use the absolute of temperature as the reference state; hence the chemical heat of dissociation will differ slightly from the spectroscopic energy of dissociation . It is a simple matter to convert from one value to the other by considering the heat capacities of the diatomic gas and the dissociated product over the range 0°K to 291°K. The former definition is invariably used in the determination of the heat of dissociation by thermochemical methods and is the one used in this paper.

During the course of a chemical reaction, bonds are broken and formed, both processes often occurring simultaneously. The need for quantitative data on dissociation energies for the study of chemical kinetics and equilibria is evident. This need has been greatly accentuated in recent years by the interest in high temperature processes resulting from the expansion of the jet propulsion field.

An unequivocal determination of the heat of dissociation of the important element fluorine has not as yet been described. In particular, experimental difficulties are encountered if attempts are made to determine the heat of dissociation of fluorine from band convergence limits either in absorption or in emission. This paper attempts to show that the "hot wire" method can be used to determine the heat of dissociation of iodine with a fair degree of accuracy, indicating that, with some refinements and minor modifications in technique, the method may be applicable for fluorine as well. Iodine was ideally suited to the experiment, since (a) its properties are similar to those of fluorine; (b) values of the dissociation energy and equilibrium constants are accurately known; and (c) the vapor pressure-temperature dependence of iodine (29.9 microns of Hg at 0°C) facilitates the establishment of a low constant bulb pressure, essential in hot wire studies.

LITERATURE SURVEY

Hot wire studies of the dissociation process fall into two broad categories--the conductometric method, in which the amount of heat carried away from the wire is measured, and the thermal equilibrium method, in which the rate of the dissociation process is determined. Langmuir (14) pioneered in the conductometric method. He observed that a stationary layer of gas seems to surround a hot wire and that heat is transferred through this layer in a pure conduction rather than convection process. For the heat carried away by conduction, Langmuir wrote

$$W_c = S(\phi_2 - \phi_1) \qquad \text{(II-1)}$$

where W_c is the rate of heat loss from a unit of surface area; S is a "shape factor" coefficient depending on the geometry of the bulb and wire and the nature of the gas; and ϕ_2 and ϕ_1 are temperature functions of the wire and bulb respectively. He further deduced that

$$S = \text{const.}\ \frac{2\pi}{\ln b/a} \qquad \text{(II-2)}$$

where b denotes the thickness of the layer of stationary gas surrounding the wire and a is the wire diameter. For ϕ_1 and ϕ_2 he wrote

$$\phi_1 = \int_0^{T_b} \lambda\, dT \quad , \quad \phi_2 = \int_0^{T_w} \lambda\, dT \qquad \text{(II-3)}$$

in which T_b is the bulb temperature, T_w is the wire temperature, and λ is the specific conductivity of the gas. He likewise deduced that $b\ \ln(b/a)$ was a constant independent of temperature and the wire diameter. These deductions were confirmed by several measurements of heat lost by hot wires under varying conditions.

When dissociation occurred, the heat lost from the wire was represented by

$$W = W_c + W_d \tag{II-4}$$

W_d being the added heat loss due to dissociation. The atoms produced at the wire were thought to diffuse away from the wire at a rate dependent on the concentration gradient dc/dx. Langmuir then concluded that

$$W_d = \frac{1}{2} QSc_oD \tag{II-5}$$

where Q is the heat of dissociation, c_o is the initial concentration of atoms in the immediate vicinity of the wire (assumed known from the temperature), and D is the gas diffusion constant for atoms in a medium of their own molecules. W_d is found by extrapolating the value of W_c in the temperature region of small dissociation and then measuring the difference between the extrapolated values and the observed total heat loss W. Q can now be determined from the variation of W_d with temperature. Using this type of calculation, Langmuir found the hydrogen bond dissociation energy to be 130 kcal/mole.

In a subsequent paper (18) Langmuir criticized the foregoing treatment, pointing out that two assumptions made were questionable: (a) that the gas in the vicinity of the wire is at the temperature of the wire and that c_o is equal to the equilibrium concentration of atoms at this temperature, and (b) that S, the shape factor, is independent of temperature over the temperature range of the experiment. The last assumption could be a serious source of error, since calculated values of Q are sensitive to small changes in S. In his revised treatment Langmuir took into account accommodation coefficients different from unity and introduced two constants, α_1 and α_2. He defined α_1 as the fraction of atoms adsorbed on the wire, and α_2 as the fraction of molecules adsorbed on the wire. He avoided the use of the shape factor S by deriving a formula for the equilibrium constant

$$K = \frac{(W/Q)^2 \; (P/D + \frac{1}{\alpha_1})^2}{P - (W/Q) \; (P/D - \frac{1}{\alpha_2})^2} \tag{II-6}$$

Values for K, D, α_1, and α_2 were chosen as those which gave best agreement between calculated and observed values of W at various pressures. Langmuir's revised values for hydrogen were $\Delta E = 84$ k cal/mole and $\Delta H = 90$ k cal/mole. The currently accepted value of the bond dissociation energy for hydrogen is 103.22 kcal/mole.

Bryce (19) measured the dissociation energy of hydrogen using the rate of dissociation method. He heated a tungsten filament in hydrogen at a pressure low enough to permit adsorption of every hydrogen atom on a layer of molybdenum oxide on the inside surface of the bulb. The rate of pressure decrease due to adsorption of the atoms thus measured the rate of dissociation. If the accommodation coefficient is assumed to be unity, the atoms and molecules leaving the wire would obey the equilibrium condition. The total mass of molecules arriving at the wire must equal the mass of particles leaving. The mass arriving is known from kinetic theory if the gas pressure and temperature are specified. An estimation of the mass of atoms produced leads directly to the equilibrium constant K for the reaction $A_2 \rightleftharpoons 2A$ at the wire temperature.

Doty (20) using Bryce's data showed that the equilibrium constant for $H_2 \rightleftharpoons 2H$ thus found agreed closely with spectroscopic data and therefore concluded that the accommodation coefficient for this system was indeed equal to one.

Mayer and Sutton (21) developed a hot wire method for the measurement of electron affinities of electronegative atoms. The electron affinity of an atom is the negative of the energy change ΔE_0 at absolute zero for the reaction

$$X_{gas} + e^-_{gas} \rightarrow X^-_{gas}$$

With their apparatus they were able to measure the current due to the flow of electrons and negative ions emitted from the hot wire and to determine separately the extent to which both species contributed to the measured current. The final computations involved the assumption that the accommodation coefficient is equal to unity for the system, iodine on tungsten.

Using the same method, Doty (22) conducted experiments to determine the C-Cℓ bond dissociation energy in methyl chloride. Assuming $a = 1$, he derived the expression

$$P_{C\ell} = \frac{i_{C\ell^-}}{i_e} \left(\frac{M_{C\ell}}{M_e}\right)^{1/2} \cdot K_2^{-1} \qquad (\text{II}-7)$$

where $K_2 = \dfrac{P_{C\ell^-}}{P_{C\ell} \cdot P_e}$ and $i_{C\ell^-}$ and i_e denote current flow due to chloride ions and electrons, respectively, and $M_{C\ell}$ and M_e denote masses of chlorine atoms and electrons, respectively. K_2 is given by known partition functions of electrons, chlorine atoms, chloride ions, in conjunction with the known electron affinity of Cl atoms. Measurement of $i_{C\ell^-}/i_e$ thus determines $P_{C\ell}$.

$P_{C\ell}$ thus leads to $K_1 = \dfrac{(P_{C\ell})^2}{P_{CH_3Cl}}$, from which the heat of dissociation can be found from the Van't Hoff Equation.

Doty found later, however, that a was appreciably less than unity for $CH_3C\ell$. A plot of $\ln K$ vs $1/T$ still appeared as a straight line for $a = 1$, from which he concluded that the "apparent" heat of reaction resulting from the use of $a = 1$ was identical with the actual heat of reaction. He was strengthened in his belief when the "apparent" heat of reaction (74 Kcal/mole) was close to the bond energy value reported by Pauling (23) at 66.5 K cal/mole and O.K. Rice (24) at 73 K cal/mole. The latter values, however, represent average bond energy rather than bond dissociation energy. The true value of the dissociation energy appears to be about 80 K cal/mole as computed from the heats of formation of methyl chloride and the methyl radical. (Cf. Reference 25).

G. Starck and M. Bodenstein (26) obtained the first reliable data on the equilibrium constant for the reaction $I_2 \rightleftharpoons 2I$ using the static manometric method. Briefly, the static manometric method is one in which a known amount of a substance is introduced into a constant volume reaction vessel and heated to a suitable temperature. After equilibrium is attained, the change in pressure is measured. The pressure change is an indication of the degree of dissociation of the substance inside the vessel. Starck and Bodenstein made their investigations over the temperature range from 800°C to 1200°C and obtained self-consistent and satisfactory results. They estimated the heat of dissociation, corrected to 0°K, at 35.5 kcal/mole. H. Baume and H. Ramstetter (27) in 1922 using the same method with a substantially lower pressure in the reaction vessel obtained the value 35.1 kcal/mole. Recently (1941) a more elaborate study of the iodine reaction was made by Perlman and Rollefson (28) employing modern techniques. Their experiments were made over the temperature range 450°C to 1000°C. They applied corrections to allow for the deviation of iodine vapor from the perfect gas law and achieved an extremely high degree of accuracy. Their value of 35.514 kcal/mole for the dissociation energy is in excellent agreement with the best spectroscopic value, 35.547 kcal/mole.

THEORY

In the analysis of the "hot wire" method for determining the heat of dissociation of iodine, the following basic assumptions are made:

(1) The vapor hitting the wire surface is an ideal gas.

(2) The equilibrium constant, K_p, for the reaction $I_2 \rightleftharpoons 2I$ occurring on the wire surface is the true equilibrium constant.

(3) The heats of adsorption and desorption of I_2 and the heat of desorption of I are negligibly small.

(4) The accommodation coefficient of iodine on platinum, a, is independent of temperature in the temperature region at which dissociation occurs.

(5) Of the total number of molecules hitting the wire the fraction a resides on the wire surface long enough to reach thermal equilibrium before leaving at the wire temperature.

The number of molecules of I_2 arriving at unit area of the wire per second and reaching thermal equilibrium at the wire temperature T_w is, from kinetic theory,

$$G = \alpha \frac{P_{I_2}}{(2\pi m_{I_2} k T_b)^{1/2}} \qquad \text{(II-8)}$$

where α is the accommodation coefficient of iodine on the wire surface, P_{I_2} is the gas pressure, and T_b is the gas temperature. Since energy changes are point functions, the expression for the energy loss per unit area per second from the wire to the adsorbed iodine molecules can be written immediately as

$$W = G\left\{ \int_{T_b}^{T_w} Cv_{I_2}\, dT + x\,\Delta E(T_w) \right\} \qquad \text{(II-9)}$$

where Cv_{I_2} is the constant volume heat capacity for iodine, $\Delta E(T_w)$ is the molar dissociation energy of iodine at temperature T_w, and x represents the percentage dissociation at temperature T_w. In the absence of dissociation, Equation (II-9) takes the simple form

$$W' = G \int_{T_b}^{T_w} Cv_{I_2}\, dT \qquad \text{(II-10)}$$

Hence, the energy loss resulting from dissociation is clearly

$$\begin{aligned} \Delta W &= W - W' \\ &= G x \Delta E(T_w) \end{aligned} \qquad \text{(II-11)}$$

and $\therefore$

$$\frac{d \ln \Delta W}{d\ ^1/_{T_w}} = \frac{d \ln x\,\Delta E(T_w)}{d\ ^1/_{T_w}} \qquad \text{(II-12)}$$

If $\overleftarrow{n}_I$ denotes the number of iodine atoms leaving unit area of the wire surface per second at equilibrium, then

$$\overleftarrow{n}_I = 2Gx$$

Similarly,

$$\overleftarrow{n}_{I_2} = G(1-x)$$

where $\overleftarrow{n}_{I_2}$ represents the rate of desorption of iodine molecules from unit area of the wire surface. Assumption (2) then allows us to write,

$$K_p(T_w) = \frac{\left(\overleftarrow{n}_I \sqrt{2\pi m_I k T_w}\right)^2}{\overleftarrow{n}_{I_2} \sqrt{2\pi m_{I_2} k T_w}} \qquad \text{(II-13)}$$

where $K_p(T_w)$ is the true equilibrium constant for the reaction $I_2 \rightleftarrows 2I$ at temperature T_w. Hence,

$$K_p(T_w) = \frac{(\overleftarrow{n}_I)^2}{\overleftarrow{n}_{I_2}} \sqrt{2\pi \frac{m_I^2}{m_{I_2}} k T_w}$$

$$= \frac{4 G x^2}{1-x} \sqrt{\pi m_I k T_w} \qquad \text{(II-14)}$$

Differentiating the logarithmic form,

$$\frac{d \ln K_p(T_w)}{d(1/T_w)} = 2\frac{d \ln x}{d(1/T_w)} - \frac{d \ln(1-x)}{d(1/T_w)} + \frac{1}{2}\frac{d \ln T_w}{d(1/T_w)}$$

$$= 2\frac{d \ln x}{d(1/T_w)} - \frac{d \ln(1-x)}{d(1/T_w)} - \frac{T_w}{2} \qquad \text{(II-15)}$$

By the Van't Hoff equation

$$\frac{d \ln K_p}{d(1/T)} = -\frac{\Delta H}{R} = -\frac{\Delta E}{R} - T \qquad \text{(II-16)} *$$

Combining Equations (II-15) and (II-16),

$$2\frac{d \ln x}{d(1/T)} - \frac{d \ln(1-x)}{d(1/T)} = -\frac{\Delta E}{R} - \frac{T}{2}$$

---

*(For convenience in writing, subscripts have been dropped. Unless otherwise stated, all temperatures refer to wire temperature T_w).

or, neglecting the small variation of ΔE with T,

$$2\frac{d\ln(x\Delta E)}{d\,{}^{1}/_{T}} = -\frac{\Delta E}{R} - \frac{T}{2} + \frac{d\ln(1-x)\Delta E}{d\,{}^{1}/_{T}} \tag{II-17}$$

Equation (II-17) when combined with Equation (II-12) yields the general result

$$2\frac{d\ln\Delta W}{d\,{}^{1}/_{T}} = -\frac{\Delta E}{R} - \frac{T}{2} + \frac{d\ln(1-x)\Delta E}{d\,{}^{1}/_{T}} \tag{II-18}$$

When x is small, Equation (II-18) reduces to

$$2\frac{d\ln\Delta W}{d\,{}^{1}/_{T}} = -\frac{\Delta E}{R} - \frac{T}{2} \tag{II-18a}$$

For values of x too large to be neglected relative to unity, Equation (II-17) can be written as

$$\frac{d\ln\Delta W}{d\,{}^{1}/_{T}} = -\frac{\Delta E}{2R} - \frac{T}{4} + \frac{d\ln(1-x)^{1/2}}{d\,{}^{1}/_{T}} \tag{II-17a}$$

or $$d\ln\frac{x}{(1-x)^{1/2}} = -\frac{\Delta E}{2R}\,d({}^{1}/_{T}) + \frac{1}{4}\,d\ln T\,; \tag{II-17b}$$

also, $$d\ln\frac{\frac{x\,\Delta E}{\Delta E}}{\left(1-\frac{x\Delta E}{\Delta E}\right)^{1/2}} = -\frac{\Delta E}{2R}\,d\frac{1}{T} + \frac{1}{4}\,d\ln T \tag{II-17c}$$

Equation (II-18a) indicates that if $\ln\Delta W - \frac{1}{4}\ln T$ is plotted against $\frac{1}{T}$, the slope of the resulting straight line is $-\frac{\Delta E}{2R}$. When ΔE has been found, x at any temperature is determined from the simple relation

$$\chi = \frac{\chi \Delta E}{\Delta E} = \frac{\Delta W}{G \Delta E} \qquad \text{(II-19)}$$

The equilibrium constant K_p is given by Equation (II-14), which for small values of x takes the simplified form

$$K_p = 2 \alpha P_{I_2} \chi^2 \left(T_w / T_b \right)^{1/2} \qquad \text{(II-14a)}$$

Finally,

$$\Delta F = - RT \ln K_p \qquad \text{(II-15)}$$

and $$\Delta S = \frac{\Delta E}{T} + R(1 + \ln K_p) \qquad \text{(II-16)}$$

EXPERIMENTAL METHOD

In the iodine heat of dissociation experiments, the technique was varied only slightly from that used in the determination of the accommodation coefficients. Crystalline iodine was introduced into a small well, W, placed in the line immediately before the entrance to the bulb (cf. PART I, Description of Apparatus). While power measurements in the vacuum were being made, the well containing the iodine was immersed in a liquid nitrogen bath. At the temperature of liquid nitrogen (80°K) the vapor pressure of iodine is substantially zero. To insure a good vacuum in the bulb, however, the system remained open to the vacuum pump. At the conclusion of the vacuum run, the liquid nitrogen bath was replaced with a distilled ice water bath. The pump was removed from the system, and the pressure was allowed to build up to 29.9 microns, the vapor pressure of iodine at 0°C. As all the available pressure reading equipment was subject to corrosive attack from the iodine vapor, it was necessary to accept the value 29.9 microns at 0°C, as given in the literature, without actual measurement of the bulb pressure.

When it was thought that the system had had sufficient time to build up to the equilibrium pressure, power was applied to the filament and measurements made over a temperature range from room temperature to about 800°K. It was found that dissociation was initiated at some temperature between 500°K and 600°K. Since the analysis was developed to make use of data taken in the region of small dissociation (cf. Theory), there was no need to raise the filament temperature above 800°K. It was, in fact, discovered that atomic iodine apparently attacks platinum, as evidenced by the steadily increasing value of the cold resistance of the filament with an increase in the amount of dissociation. Measurements made at the higher filament temperatures would be extremely questionable if not valueless.

Calculation of ΔE, the Heat of Dissociation

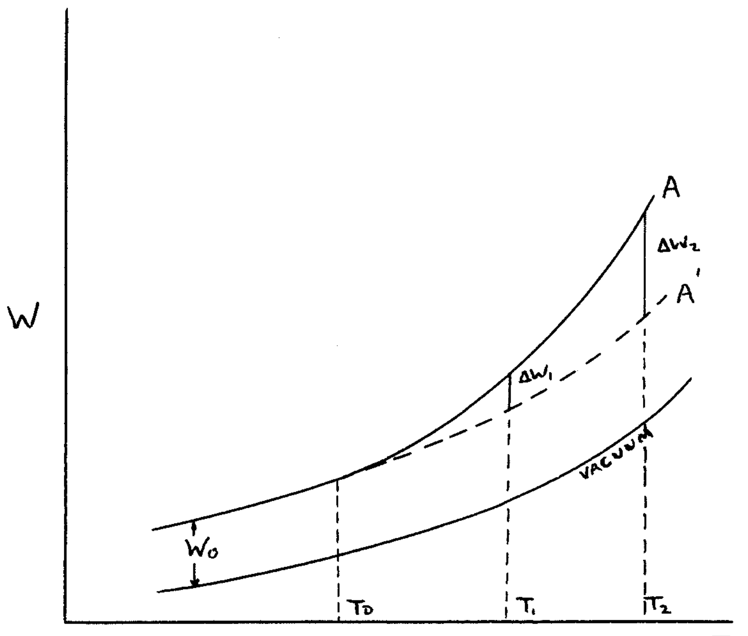

Figure 7

If a filament is immersed in a gas which dissociates appreciably above some temperature T_D at a given pressure, a plot of power loss versus filament temperature will result in a curve of the type labelled A in Fig. 7. In the region of temperatures less than T_D, previous analysis has shown that

$$W_o = \alpha W_T = \alpha \frac{\pi p l d k}{(2\pi m k T_b)^{1/2}} \int_{T_b}^{T_w} (\beta + \tfrac{1}{2})\, dT \qquad \text{(I-16)}$$

where W_o = observed power loss, the difference between the loss in the gas and the loss in the vacuum.

W_T = theoretical or ideal power loss based on the assumption that all molecules reach thermal equilibrium with the filament.

α = accommodation coefficient for the gas-metal system.

Above temperature T_D, the gas dissociates and the relation (I-16) no longer holds, since the dissociating molecules remove an added amount of energy from the filament. If, upon assuming a constant value of α, Equation (I-16) is used to calculate values of W_o at temperatures exceeding T_D, the hypothetical curve A' may be constructed. Curve A' represents the power loss to the gas which would obtain with no dissociation. Hence the difference between the two curves A and A' at any temperature is a measure of the extra energy removal due solely to dissociation, ΔW. The assumption of constant α has been shown by experimental evidence to be a valid one for non-dissociating molecules (cf. PART I).

In the analysis given previously in the section on theory it was seen that if the quantity $\ln \Delta W - \frac{1}{4} \ln T_w$ is plotted against $1/T_w$ the result for small values of x is a straight line of slope $-\Delta E/2R$. Several values of ΔW versus T_w in the low dissociation region are taken from the curves of Figure 7 and the curve, Figure 8 is constructed. The heat of dissociation, ΔE, is thus readily found from the slope of this line.

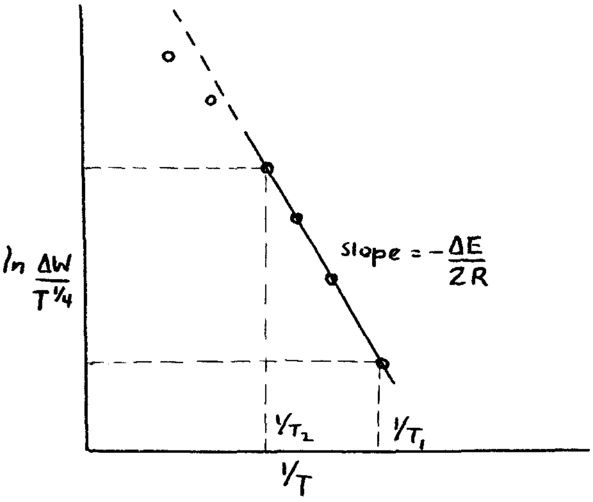

Figure 8

Since the analysis was developed for small values of x, it can be expected that the curve will show a decrease in slope at the higher temperatures where x is no longer small.

INTERPRETATION OF RESULTS

The accommodation coefficient of iodine on platinum, calculated from the curves of Figure 26, was found to have a constant value of .82 for filament temperatures ranging from 400°K to 600°K. Since dissociation becomes appreciable at a filament temperature of roughly 600°K, as evidenced by a significant increase in filament power loss at this temperature, the value $\alpha = .82$ was used for the construction of the hypothetical "no-dissociation" heat loss curve of Figure 27. ΔW values at several temperatures were obtained from Figure 27 for use in plotting the logarithmic curve Figure 28, whose slope is proportional to the heat of dissociation. Measurement of this slope between the temperatures 600°K and 700°K gives $\Delta E = 36.9$ Kcal/mole. The amounts of dissociation at each temperature are found from Equation (II-19); at $T_w = 600°K$, $x = .018$ and at $T_w = 700°K$, $x = .064$. The equilibrium constant, the entropy change, and the free energy change are given by Equations (II-14a), (II-16), and (II-15) respectively. These values are compared with values computed from data presented in the National Bureau of Standards, Tables of Selected Values of Chemical Thermodynamic Properties, Series III, Volume I.

		NBS Tables	Experimental
ΔE	600°K	35.17 Kcals/mole	36.9 Kcal/mole
	700°K	35.04 Kcals/mole	
K_p	600°K	1.46×10^{-8}	2.98×10^{-8}
	700°K	115.02×10^{-8}	40.70×10^{-8}
ΔS	600°K	24.81 cals/mole	29.1 cals/mole
	700°K	24.95 cals/mole	25.4 cals/mole
ΔF	600°K	21.44 Kcals/mole	20.58 Kcal/mole
	700°K	18.97 Kcals/mole	20.40 Kcals/mole

TABLE 7

The value 36.9 kcal/mole for the heat of dissociation is in error by 4.8 % from the accepted value. It should be possible to reduce this error by making additional refinements to the apparatus, which was originally designed for the measurement of accommodation coefficients. Such refinements should include equipment capable of providing accurate determinations of the pressure of the iodine vapor in the bulb. During the experiments with the present apparatus it was necessary to assume that equilibrium between the iodine crystals in the ice water bath and the iodine vapor had been reached after a suitable period of time had elapsed. Equilibrium would be positively indicated by a pressure gage.

Another probable source of error is the assumption that the equilibrium constant for the reaction $I_2 \rightleftarrows 2I$ occurring on the metal surface is identical with the equilibrium constant for the same reaction occurring in the gas.

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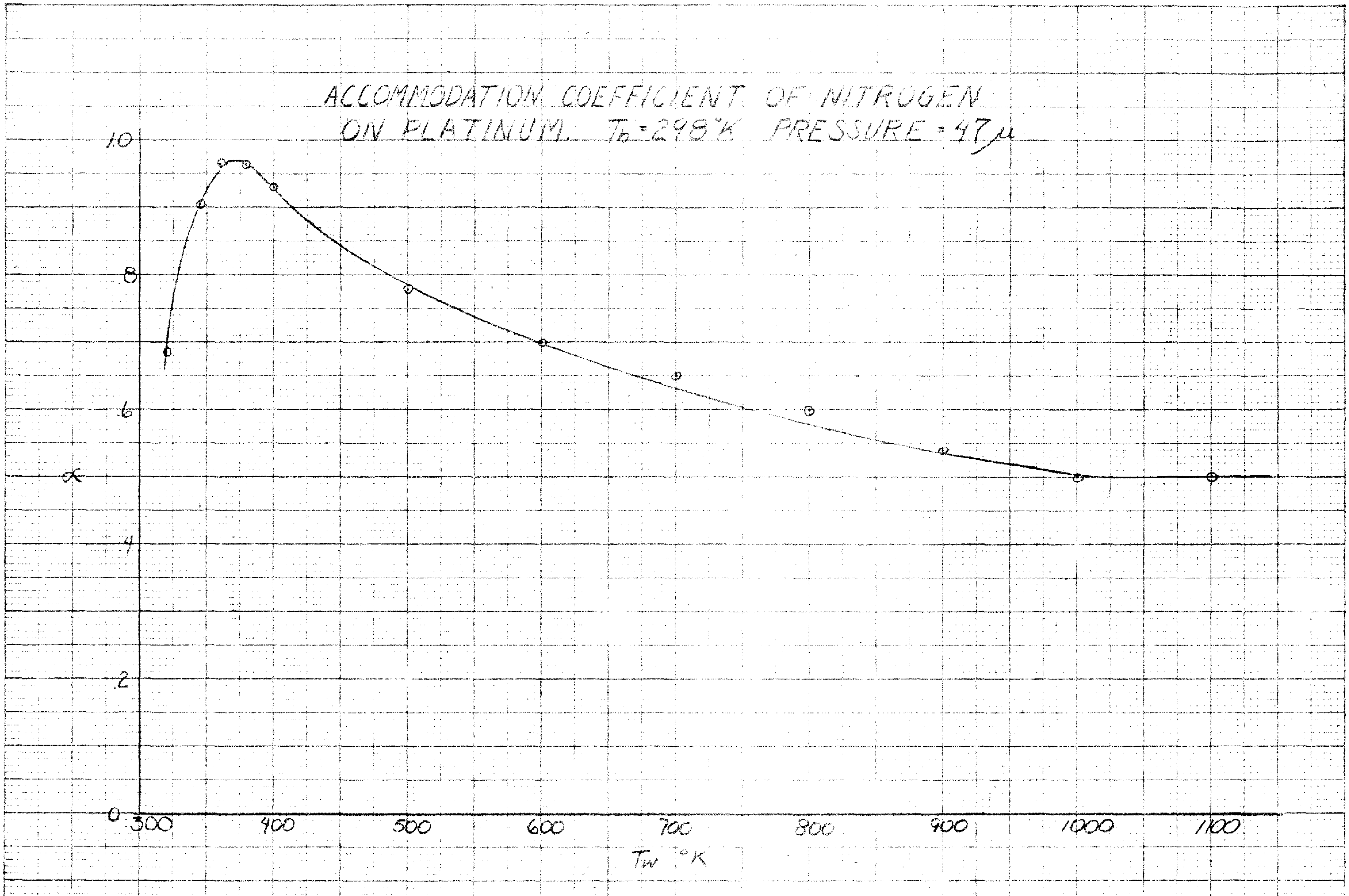


ACCOMMODATION COEFFICIENT OF NITROGEN ON PLATINUM. $T_b = 298°K$ PRESSURE = 47μ

FIGURE 9

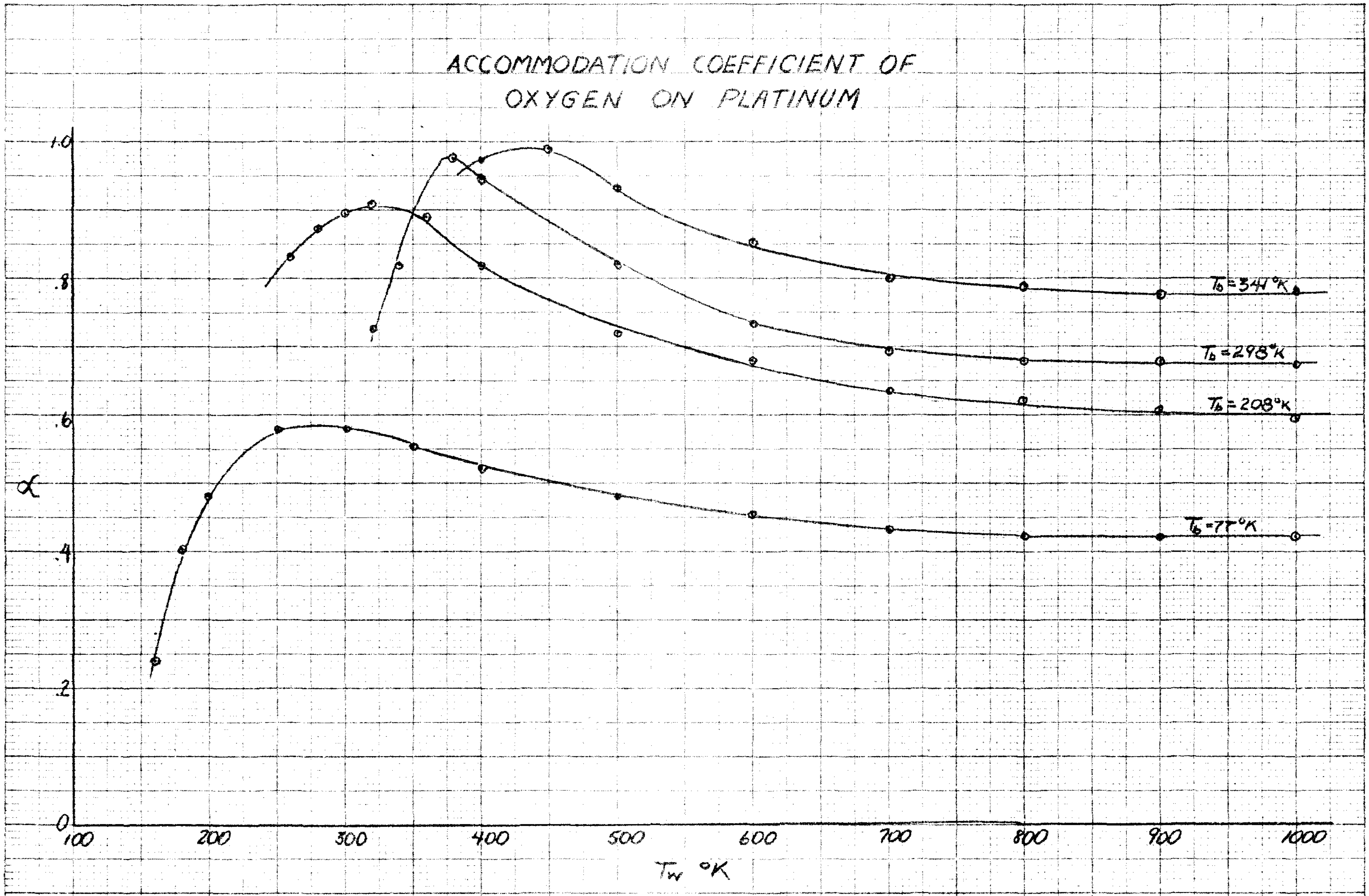
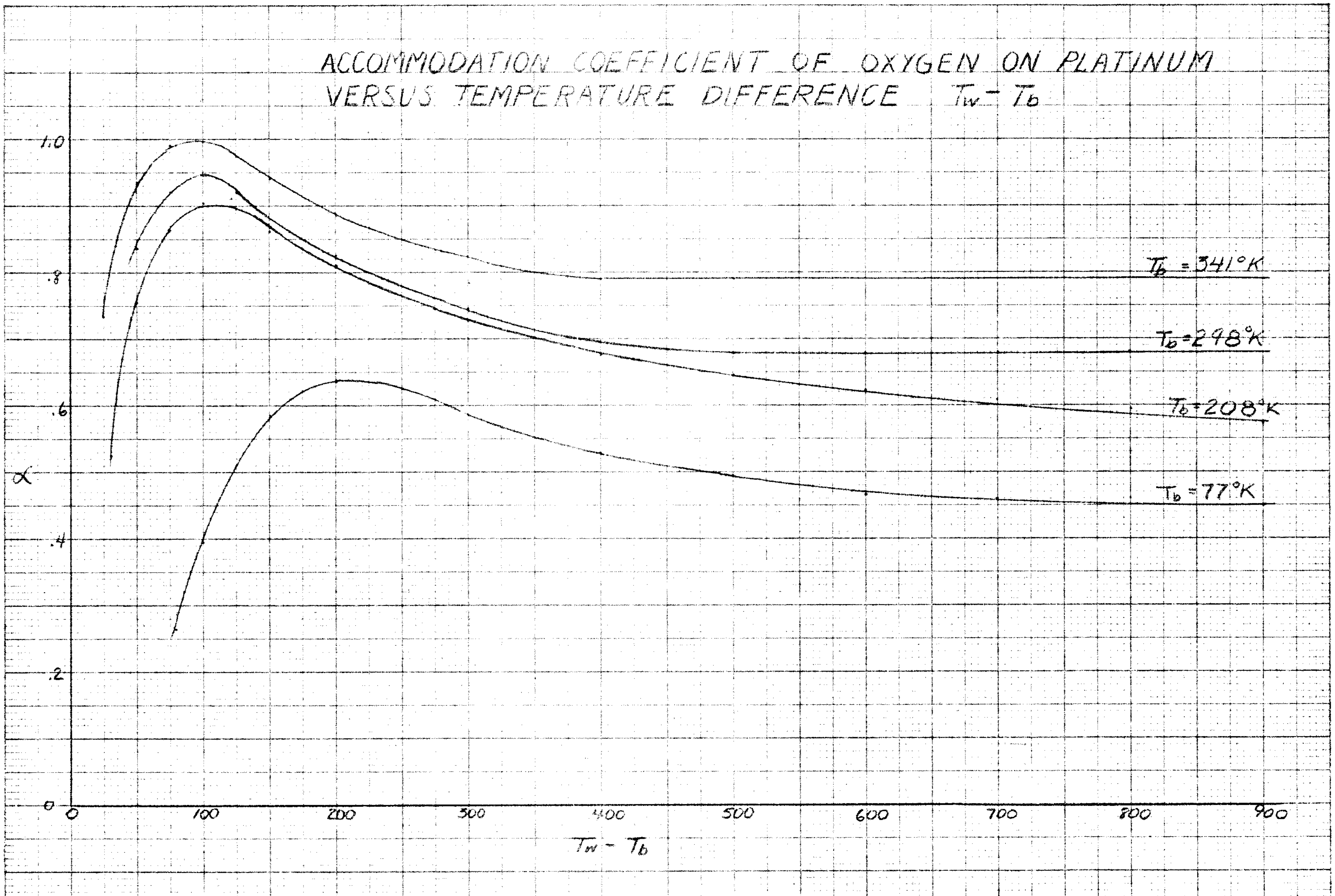

ACCOMMODATION COEFFICIENT OF
OXYGEN ON PLATINUM
α
1.0
.8
.6
.4
.2
0
100
200
300
400
500
600
700
800
900
1000
Tw °K
Tb = 341°K
Tb = 298°K
Tb = 208°K
Tb = 77°K

FIGURE 10



ACCOMMODATION COEFFICIENT OF OXYGEN ON PLATINUM VERSUS TEMPERATURE DIFFERENCE $T_w - T_b$

FIGURE 11

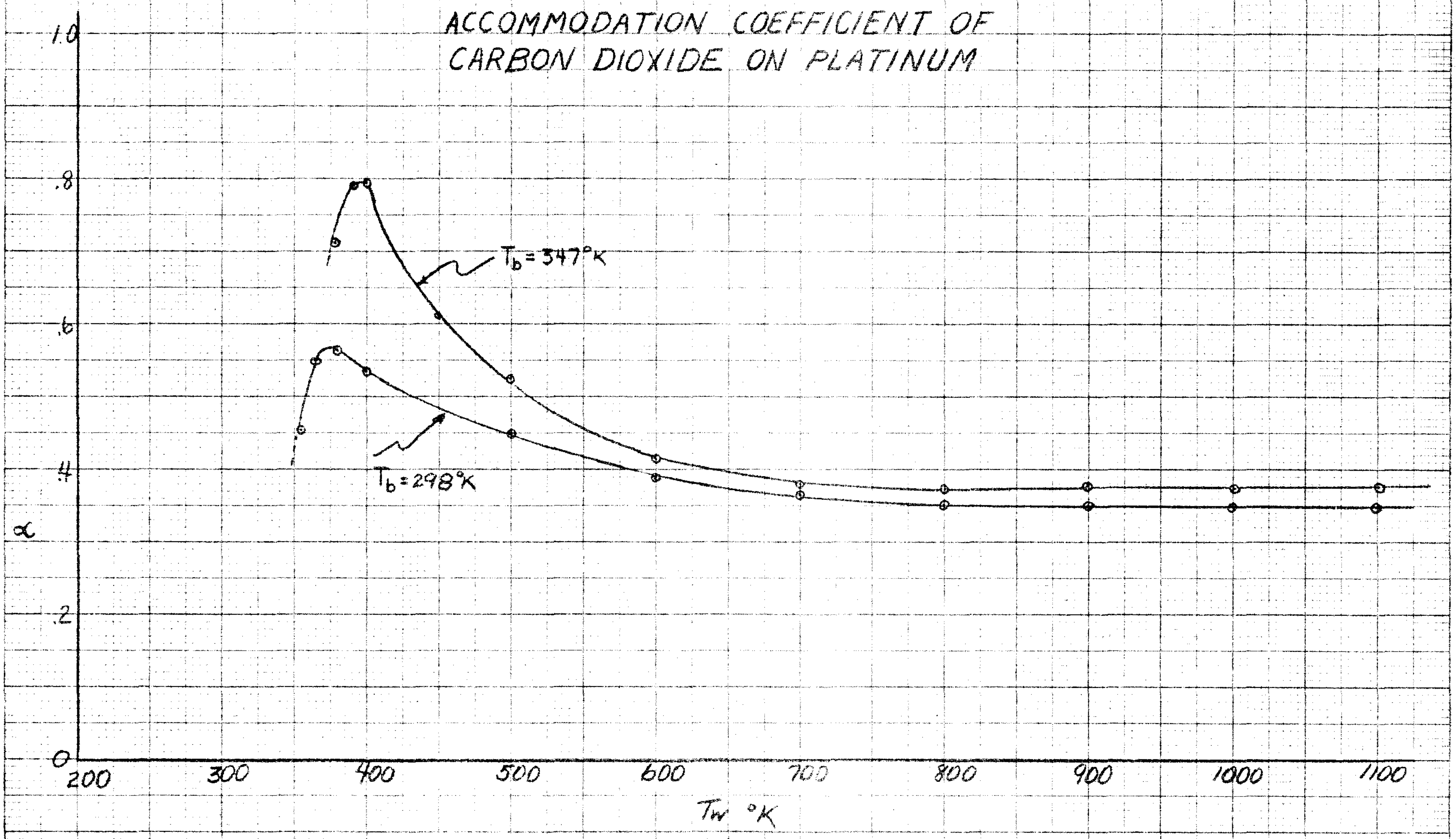

ACCOMMODATION COEFFICIENT OF
CARBON DIOXIDE ON PLATINUM
1.0
.8
.6
.4
.2
0
α
200
300
400
500
600
700
800
900
1000
1100
Tw °K
Tb = 347°K
Tb = 298°K

FIGURE 12

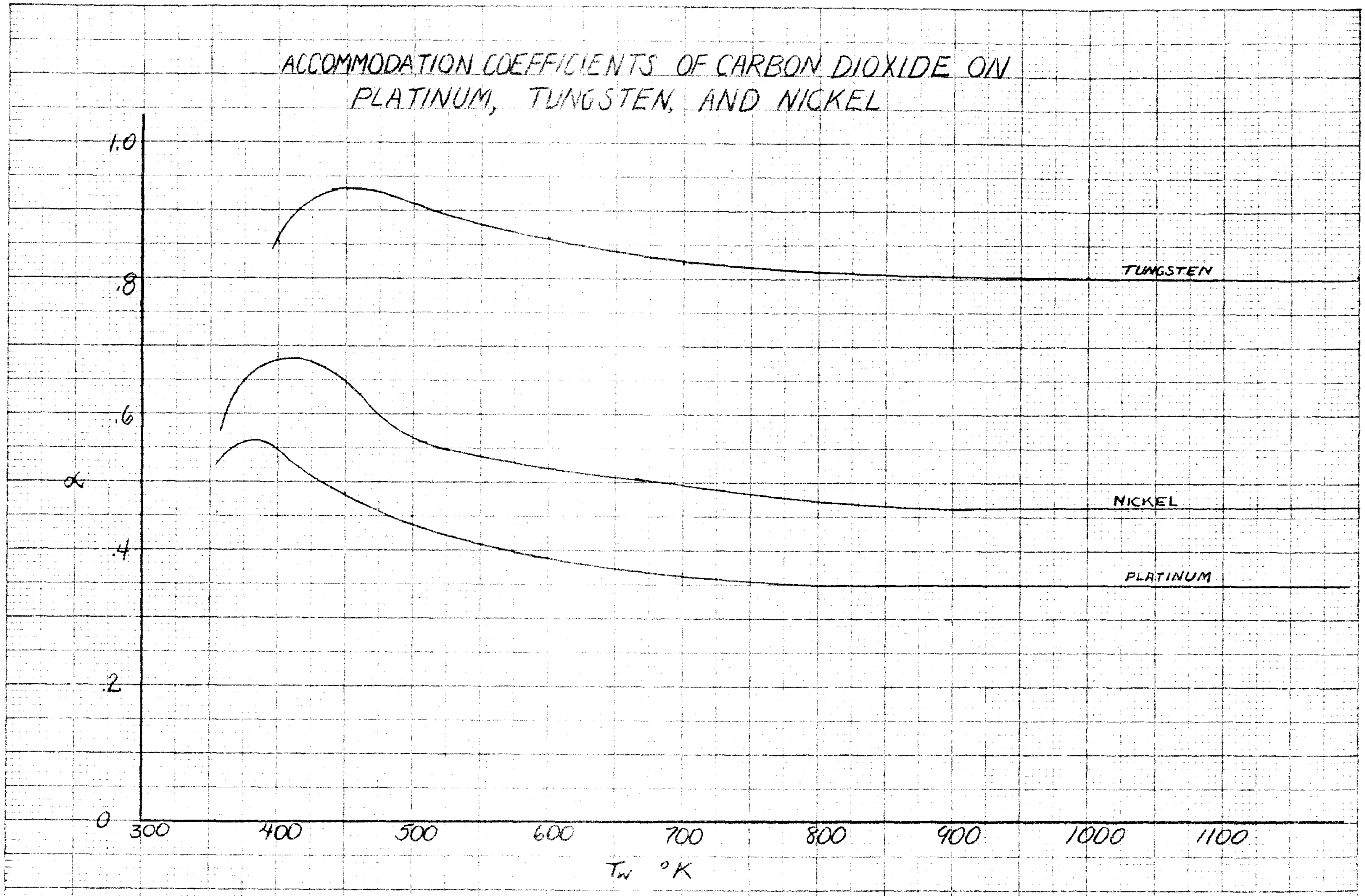

ACCOMMODATION COEFFICIENTS OF CARBON DIOXIDE ON PLATINUM, TUNGSTEN, AND NICKEL

FIGURE 13

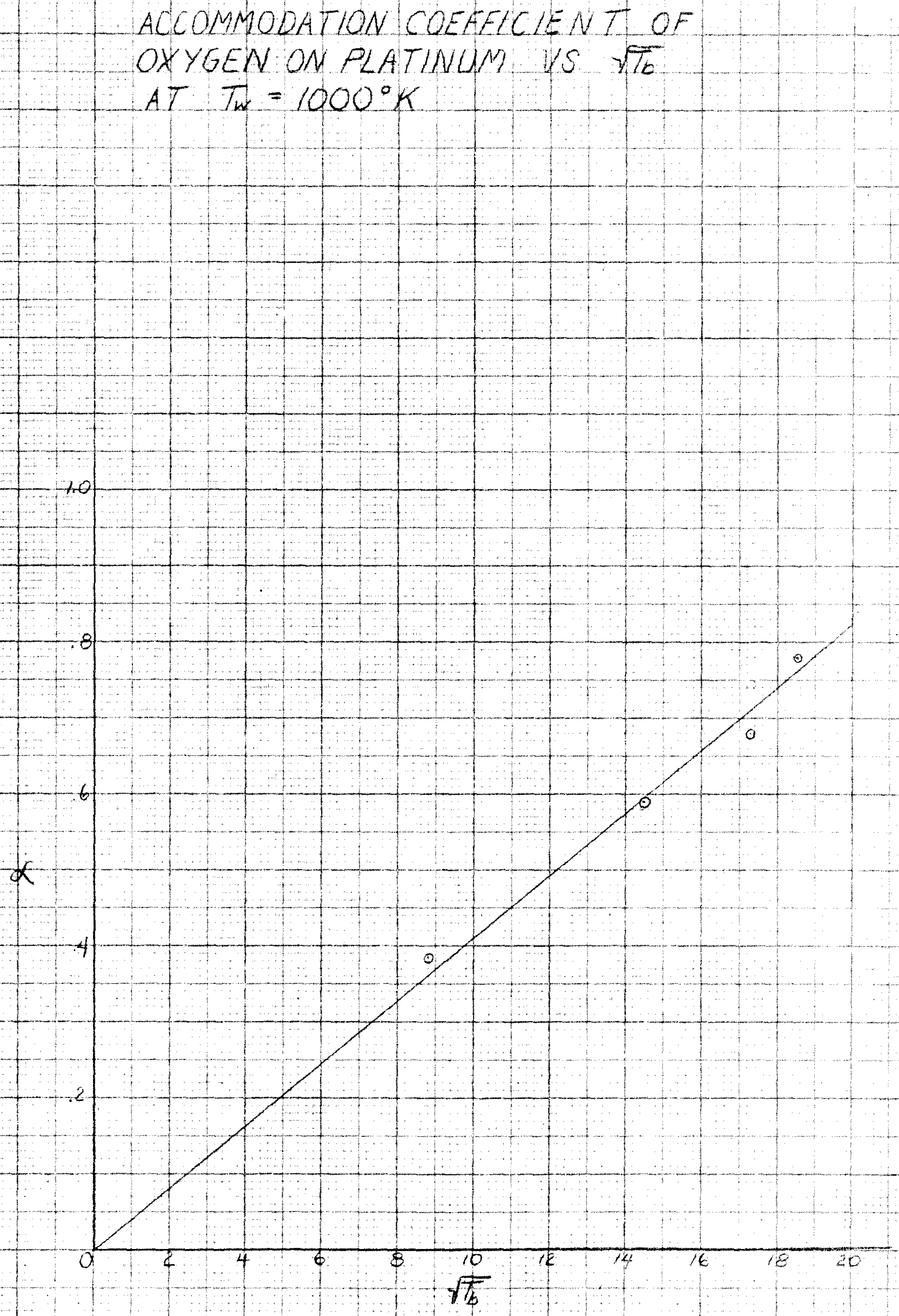

ACCOMMODATION COEFFICIENT OF
OXYGEN ON PLATINUM VS $\sqrt{T_b}$
AT T_w = 1000°K
1.0
.8
.6
.4
.2
α
0
2
4
6
8
10
12
14
16
18
20
$\sqrt{T_b}$

FIGURE 14

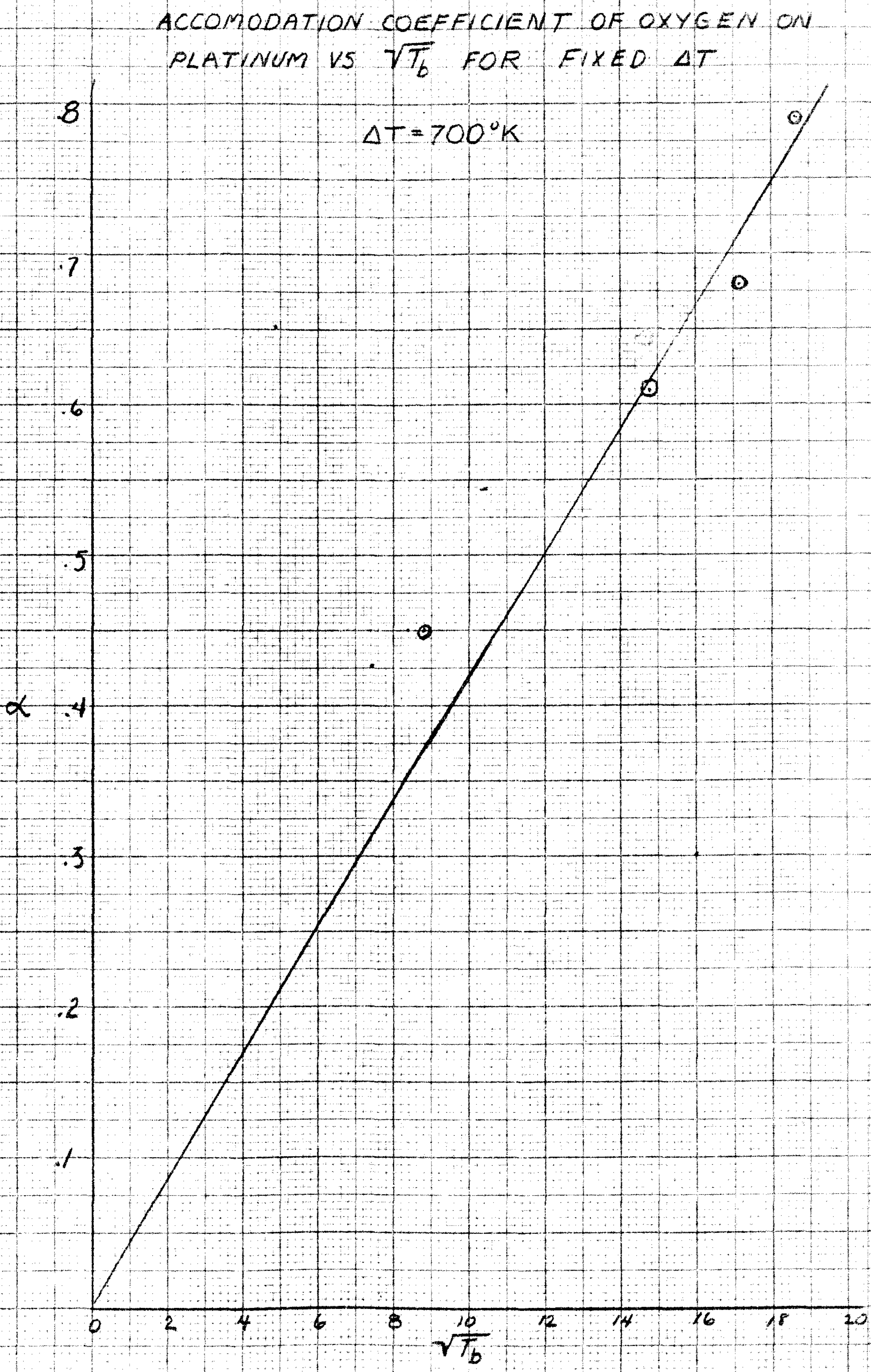

ACCOMODATION COEFFICIENT OF OXYGEN ON PLATINUM VS $\sqrt{T_b}$ FOR FIXED ΔT
$\Delta T = 700°K$
α
.1
.2
.3
.4
.5
.6
.7
.8
0
2
4
6
8
10
12
14
16
18
20
$\sqrt{T_b}$

FIGURE 15

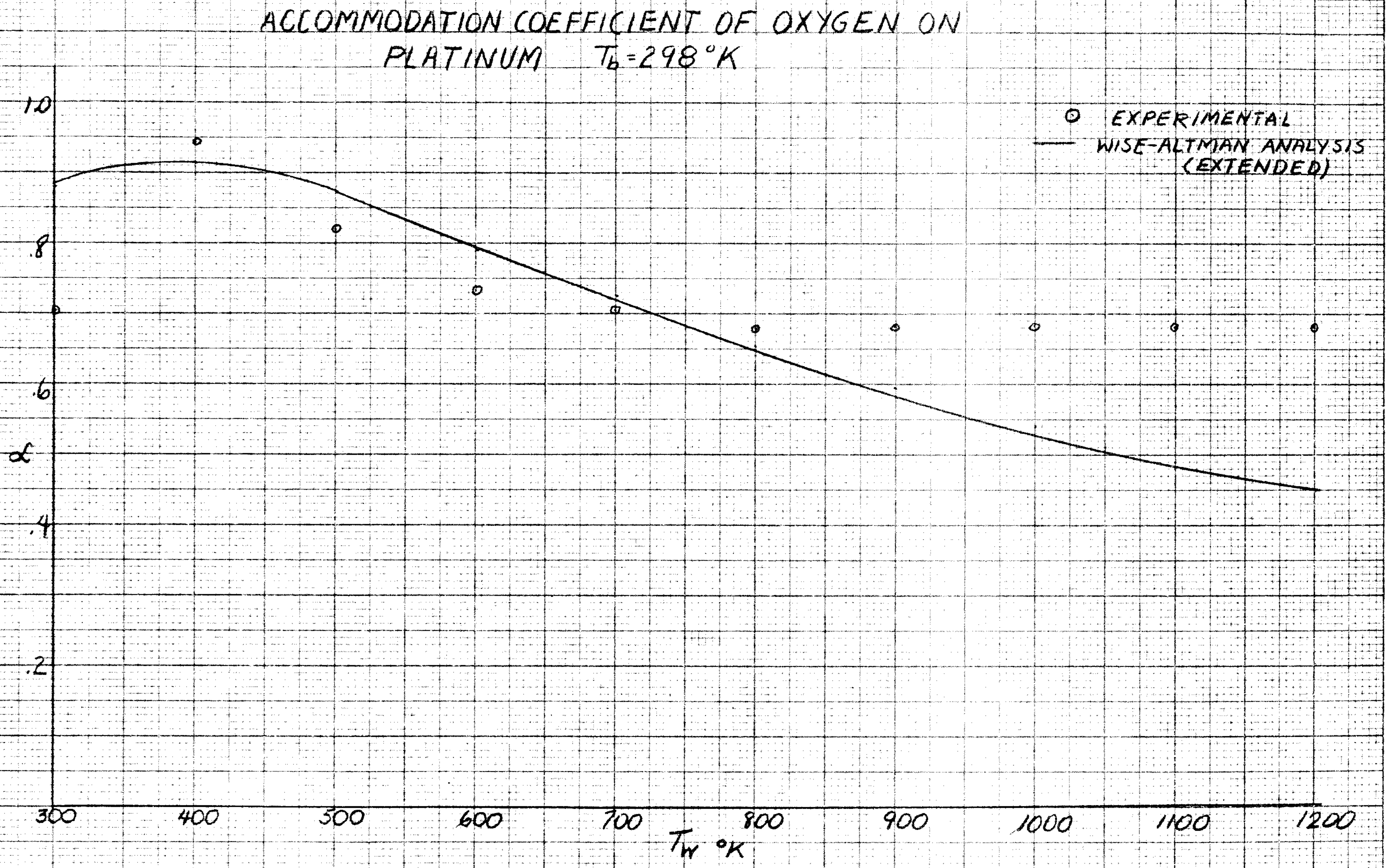

ACCOMMODATION COEFFICIENT OF OXYGEN ON
PLATINUM $T_b = 298°K$
1.0
.8
.6
.4
.2
α
300
400
500
600
700
800
900
1000
1100
1200
T_W °K
EXPERIMENTAL
WISE-ALTMAN ANALYSIS (EXTENDED)

FIGURE 16-a

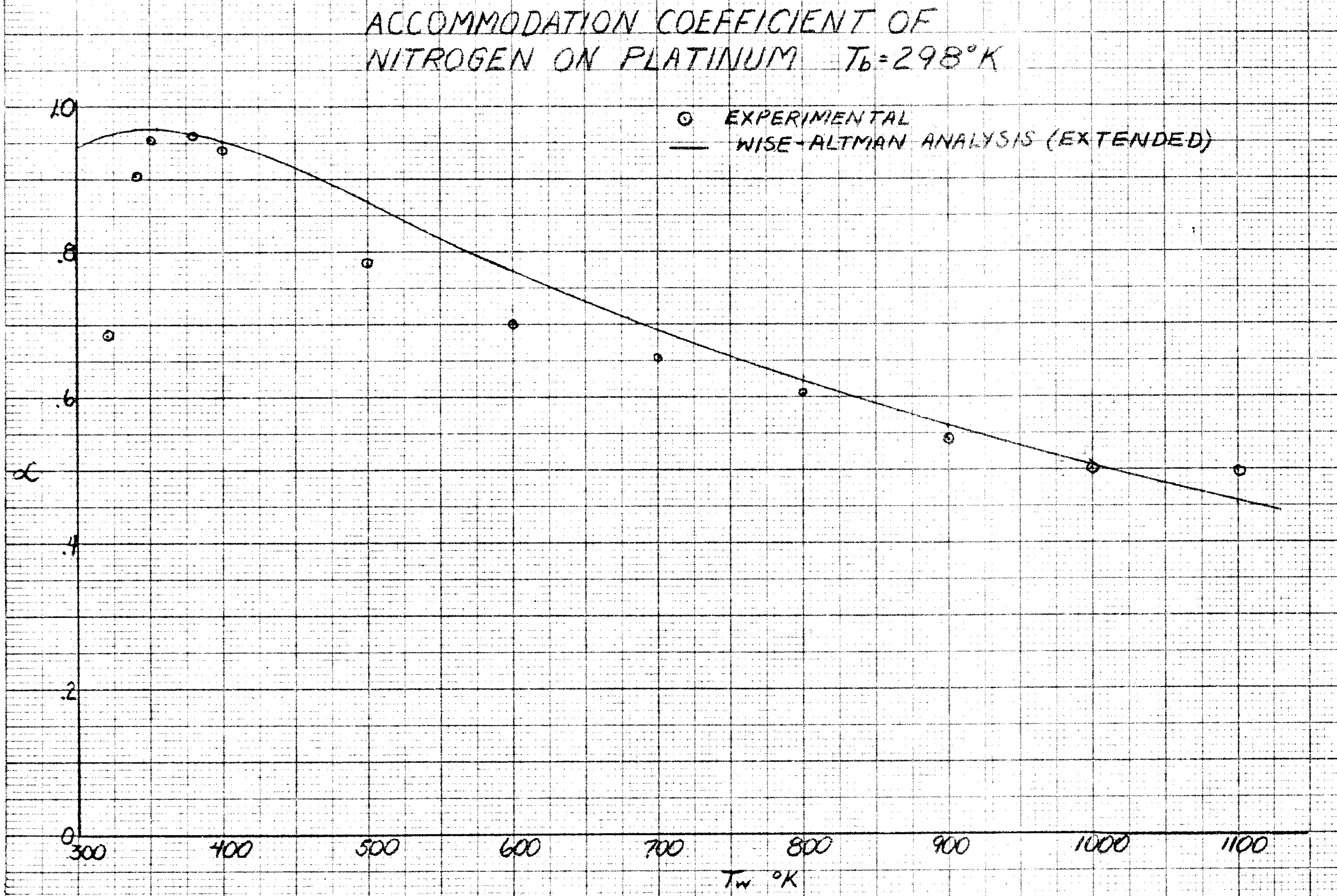

ACCOMMODATION COEFFICIENT OF
NITROGEN ON PLATINUM T_b=298°K
EXPERIMENTAL
WISE-ALTMAN ANALYSIS (EXTENDED)
1.0
.8
.6
.4
.2
0
α
300
400
500
600
700
800
900
1000
1100
T_w °K

FIGURE 16-b

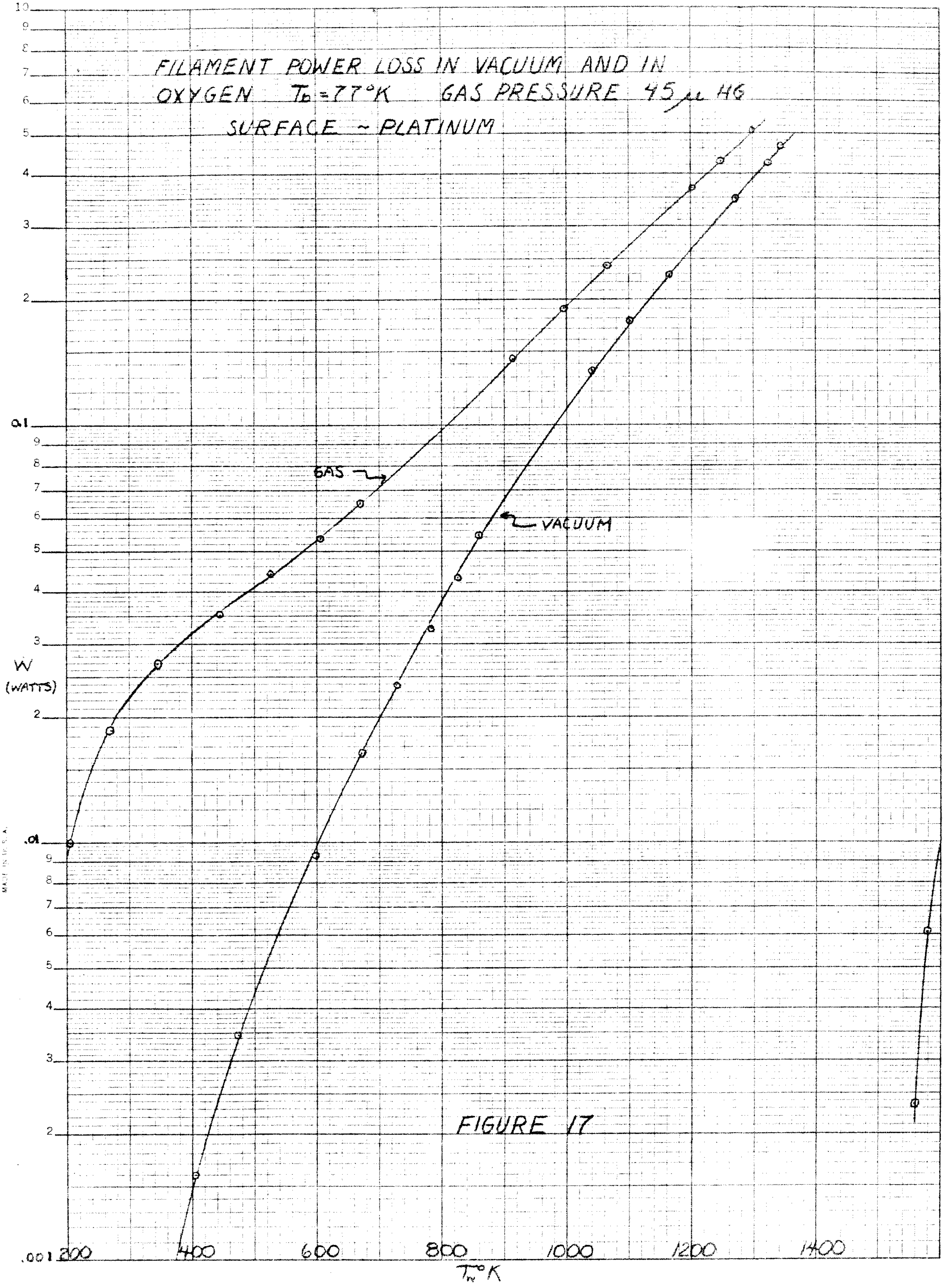
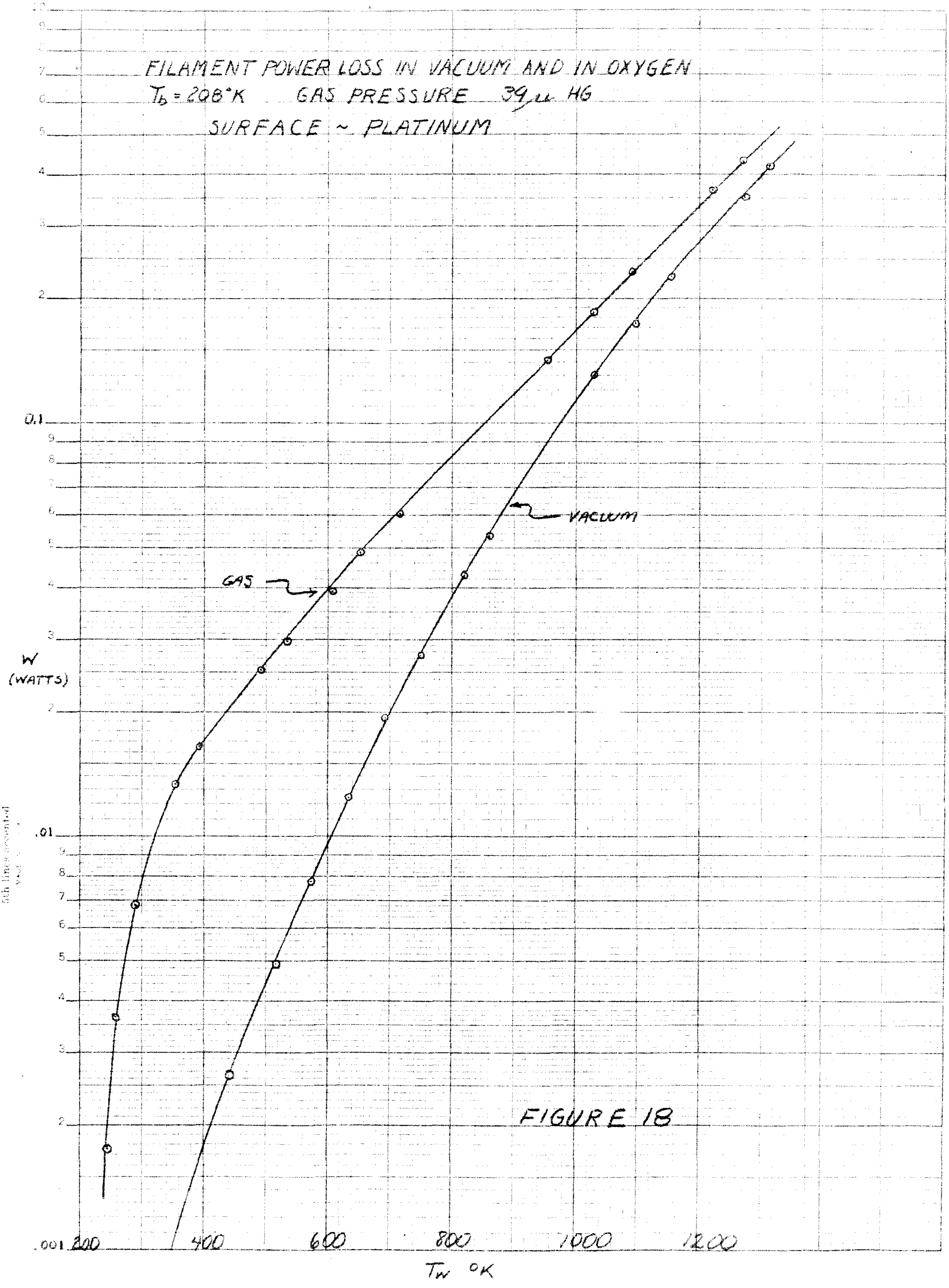

FILAMENT POWER LOSS IN VACUUM AND IN
OXYGEN $T_b = 77°K$ GAS PRESSURE 45 μ HG
SURFACE ~ PLATINUM
GAS
VACUUM
W
(WATTS)
10
9
8
7
6
5
4
3
2
0.1
9
8
7
6
5
4
3
2
.01
9
8
7
6
5
4
3
2
.001
200
400
600
800
1000
1200
1400
T_w°K

FIGURE 17



FILAMENT POWER LOSS IN VACUUM AND IN OXYGEN
$T_b = 298°K$ GAS PRESSURE 39 μ HG
SURFACE ~ PLATINUM

FIGURE 18

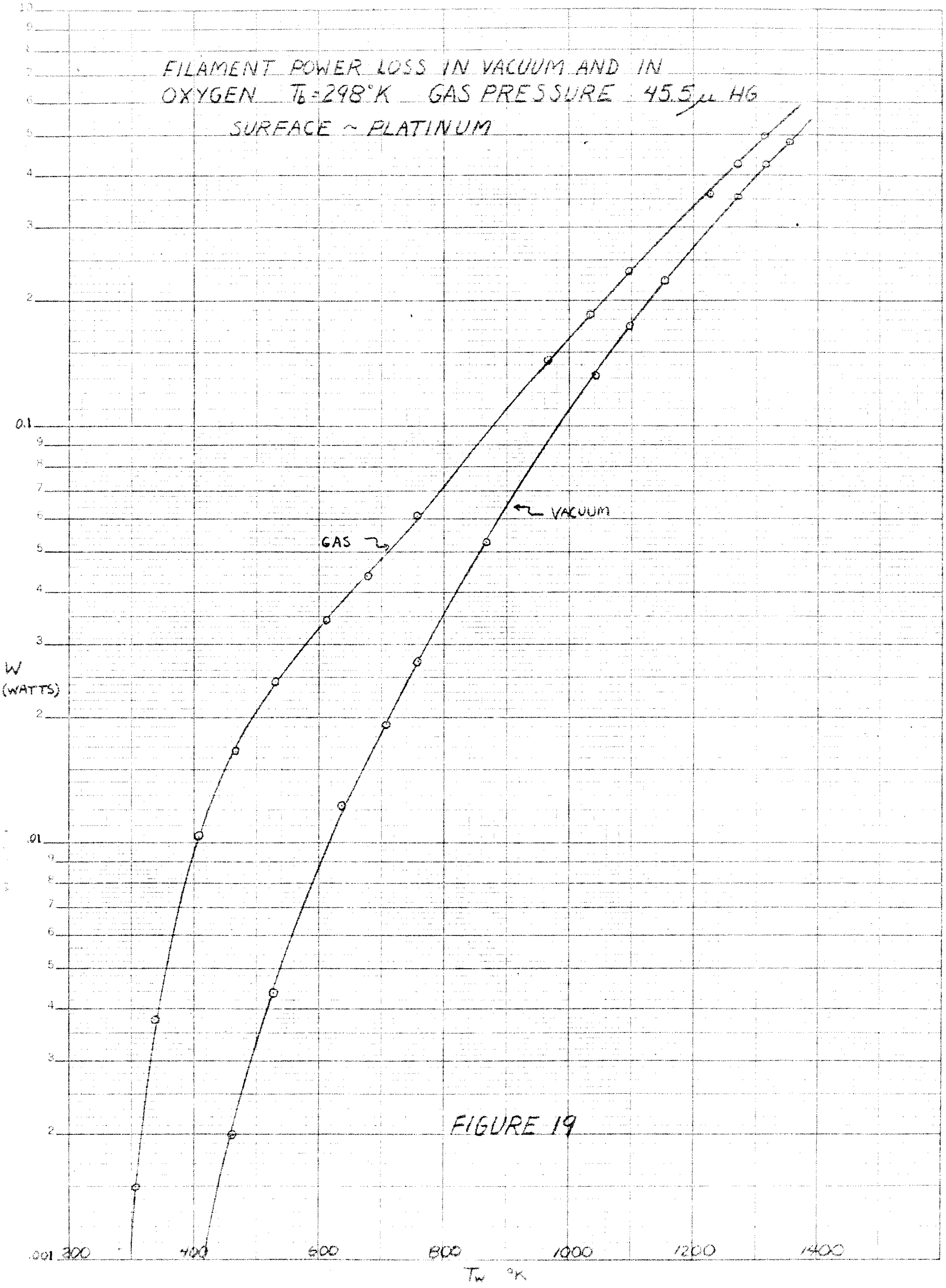

FILAMENT POWER LOSS IN VACUUM AND IN
OXYGEN $T_b = 298°K$ GAS PRESSURE 45.5 μ HG
SURFACE ~ PLATINUM
GAS
VACUUM
W
(WATTS)
0.1
.01
.001
300
400
600
800
1000
1200
1400
T_w °K

FIGURE 19

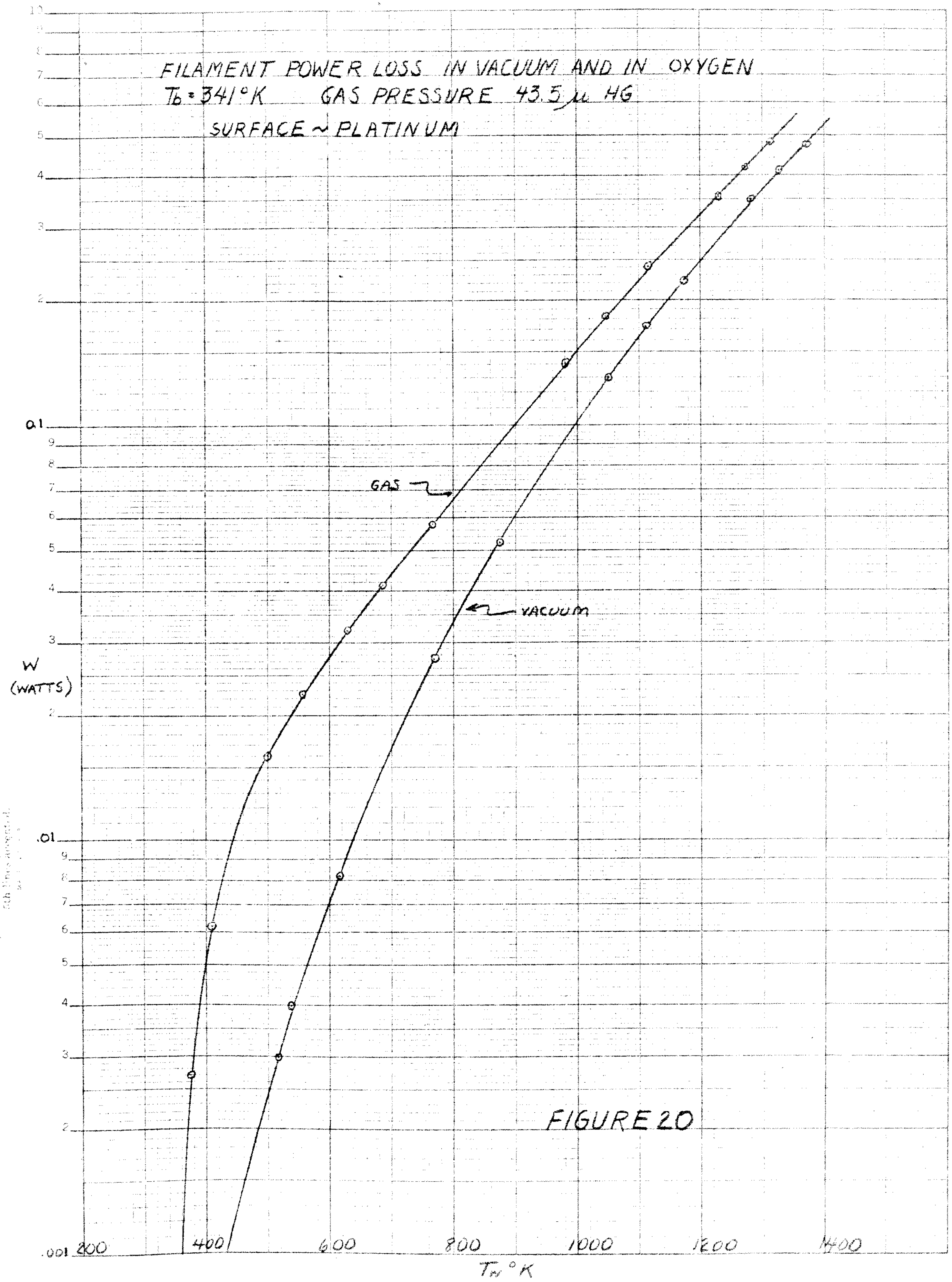
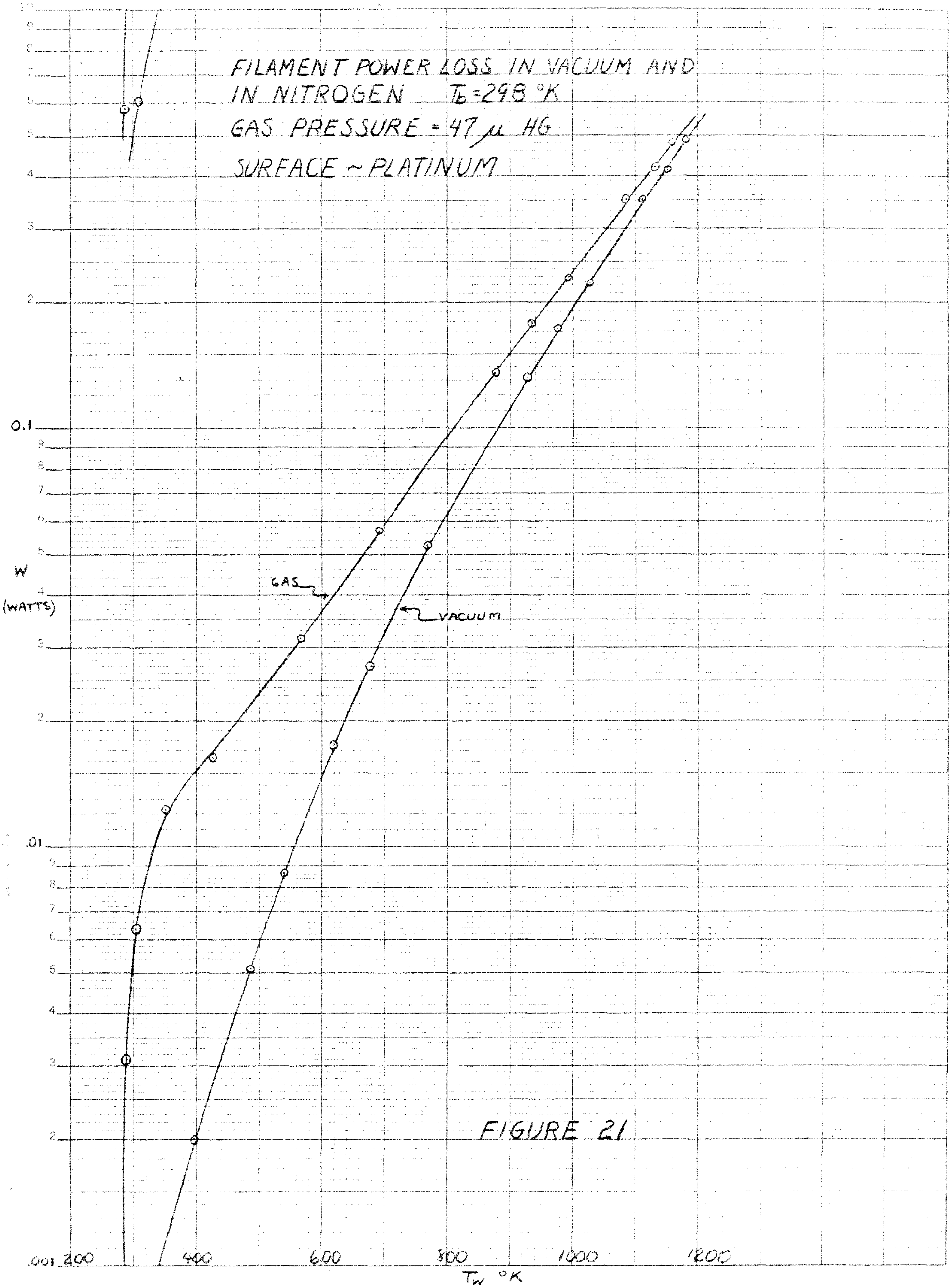

FILAMENT POWER LOSS IN VACUUM AND IN OXYGEN
$T_b = 341°K$ GAS PRESSURE 43.5 μ HG
SURFACE ~ PLATINUM
GAS
VACUUM
W (WATTS)
0.1
.01
.001
200
400
600
800
1000
1200
1400
T_w °K

FIGURE 20

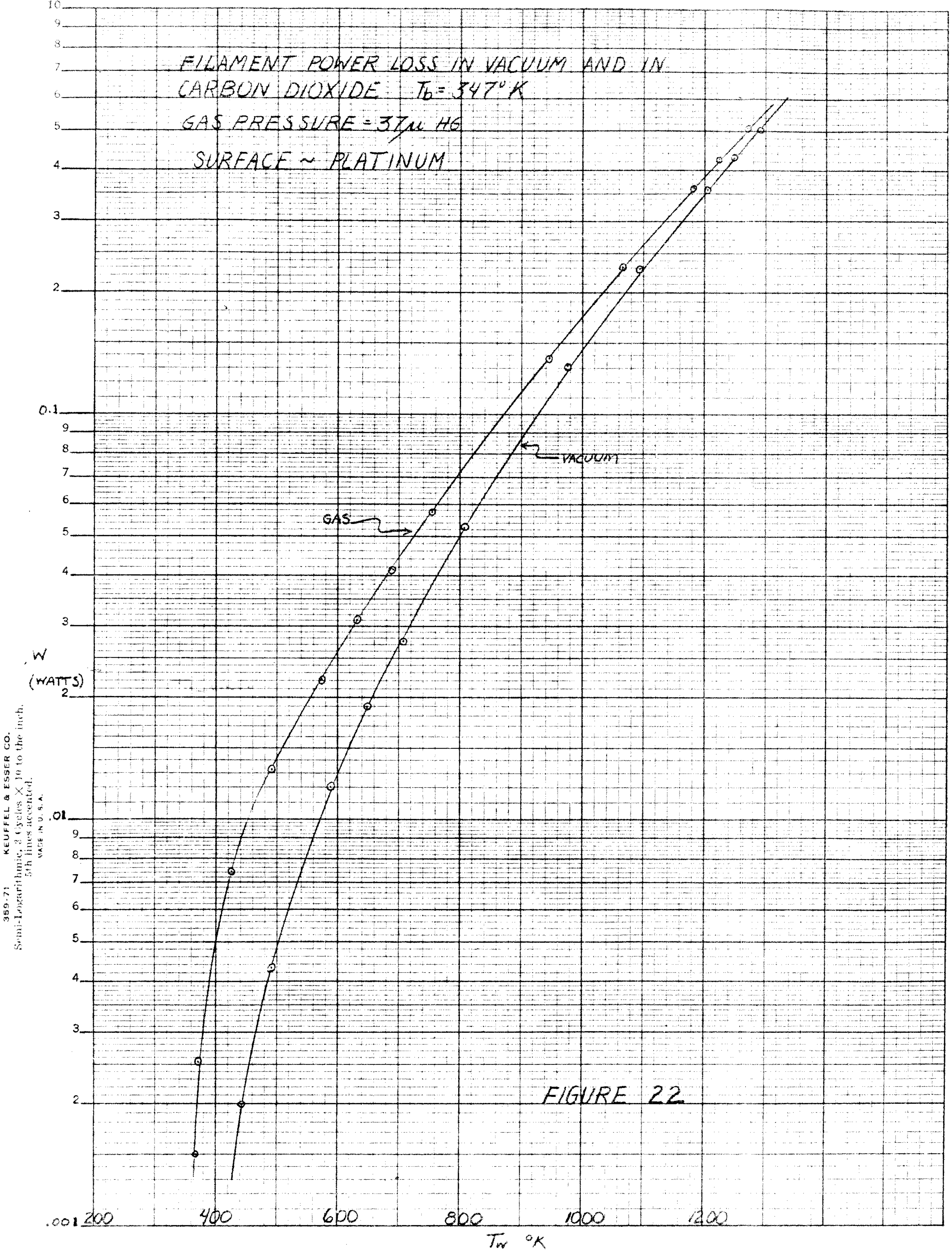


FILAMENT POWER LOSS IN VACUUM AND IN NITROGEN $T_b = 298$ °K

GAS PRESSURE = 47 μ HG

SURFACE ~ PLATINUM

FIGURE 21



FILAMENT POWER LOSS IN VACUUM AND IN CARBON DIOXIDE $T_b = 347°K$

GAS PRESSURE = 37 μ HG

SURFACE ~ PLATINUM

FIGURE 22

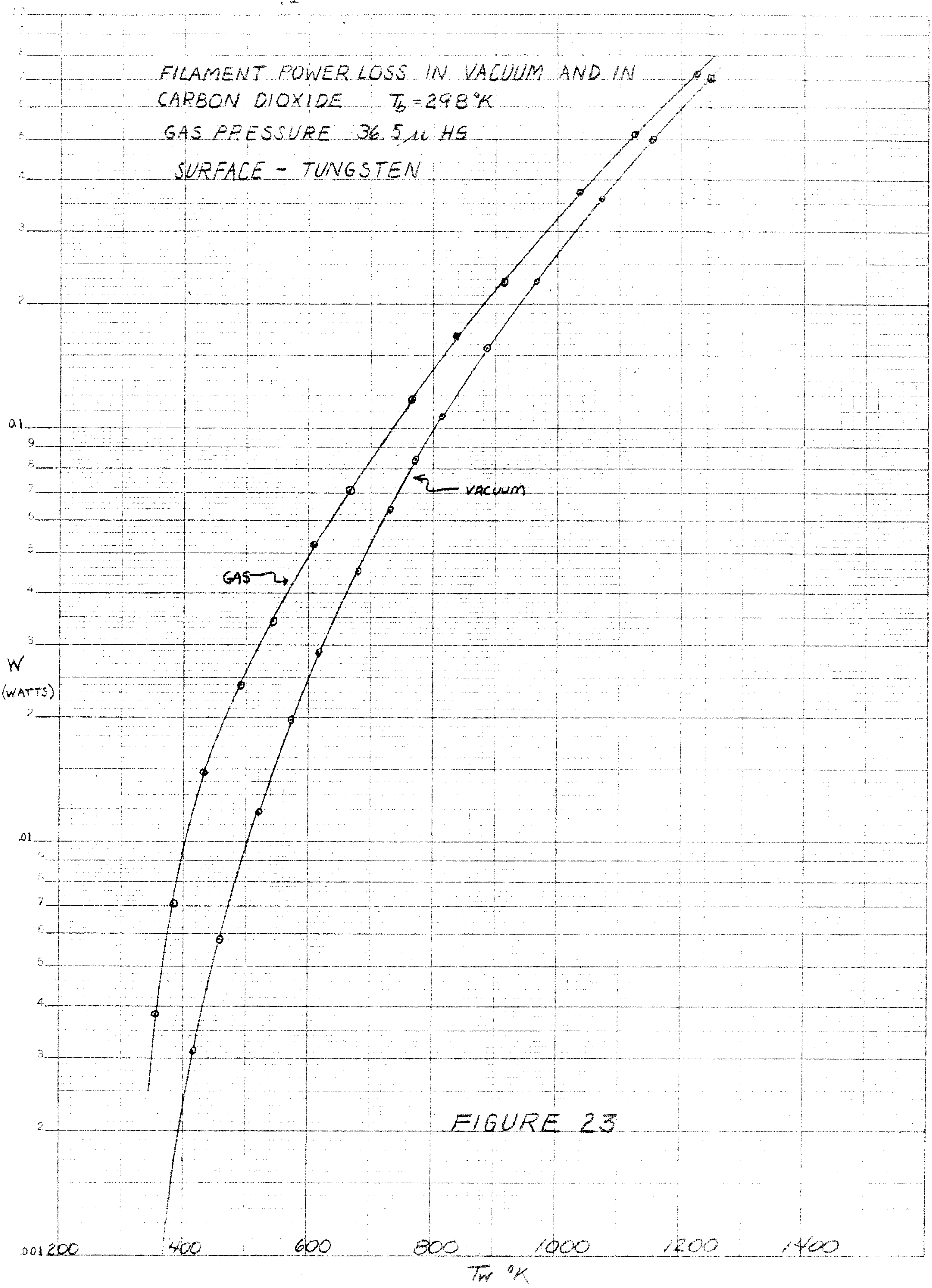

FILAMENT POWER LOSS IN VACUUM AND IN
CARBON DIOXIDE T_b = 298°K
GAS PRESSURE 36.5 μ HG
SURFACE - TUNGSTEN
VACUUM
GAS
W
(WATTS)
.1
.01
.001
200
400
600
800
1000
1200
1400
Tw °K

FIGURE 23

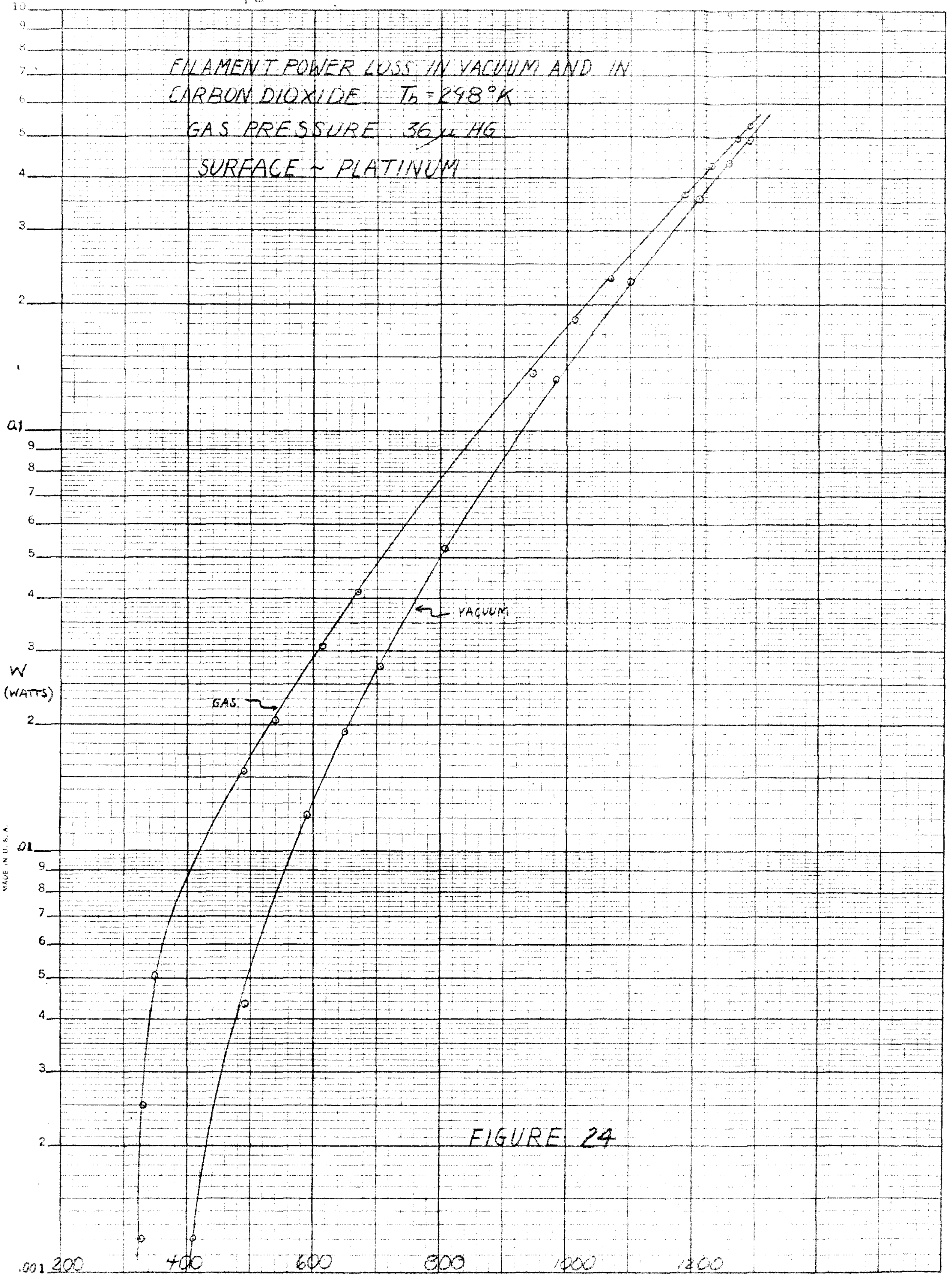
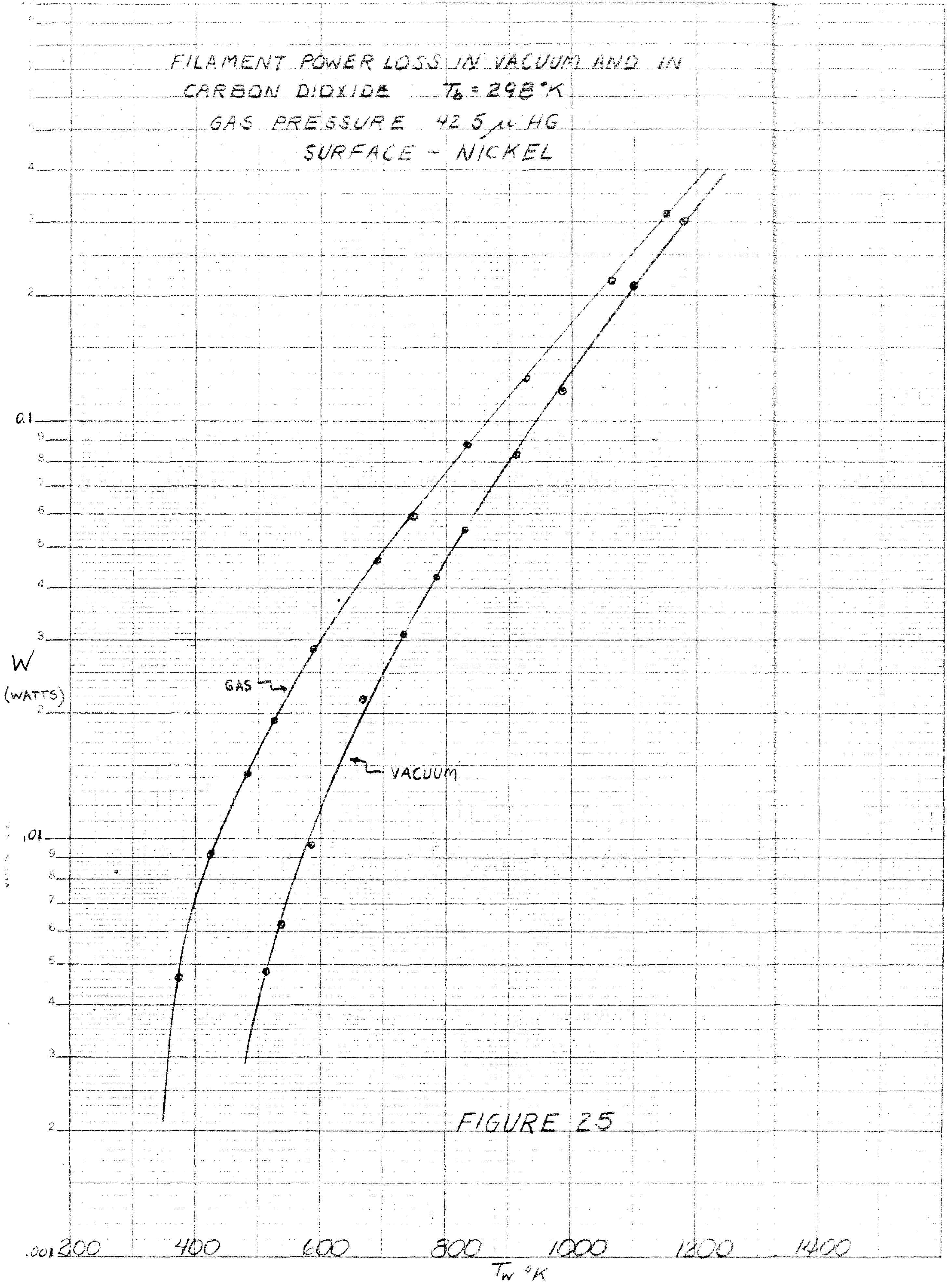

FILAMENT POWER LOSS IN VACUUM AND IN
CARBON DIOXIDE $T_b = 298°K$
GAS PRESSURE 36 μ HG
SURFACE ~ PLATINUM
VACUUM
GAS
W
(WATTS)
10
9
8
7
6
5
4
3
2
0.1
9
8
7
6
5
4
3
2
.01
9
8
7
6
5
4
3
2
.001
200
400
600
800
1000
1200

FIGURE 24



FILAMENT POWER LOSS IN VACUUM AND IN CARBON DIOXIDE $T_b = 298°K$

GAS PRESSURE 42.5 μ HG

SURFACE ~ NICKEL

FIGURE 25

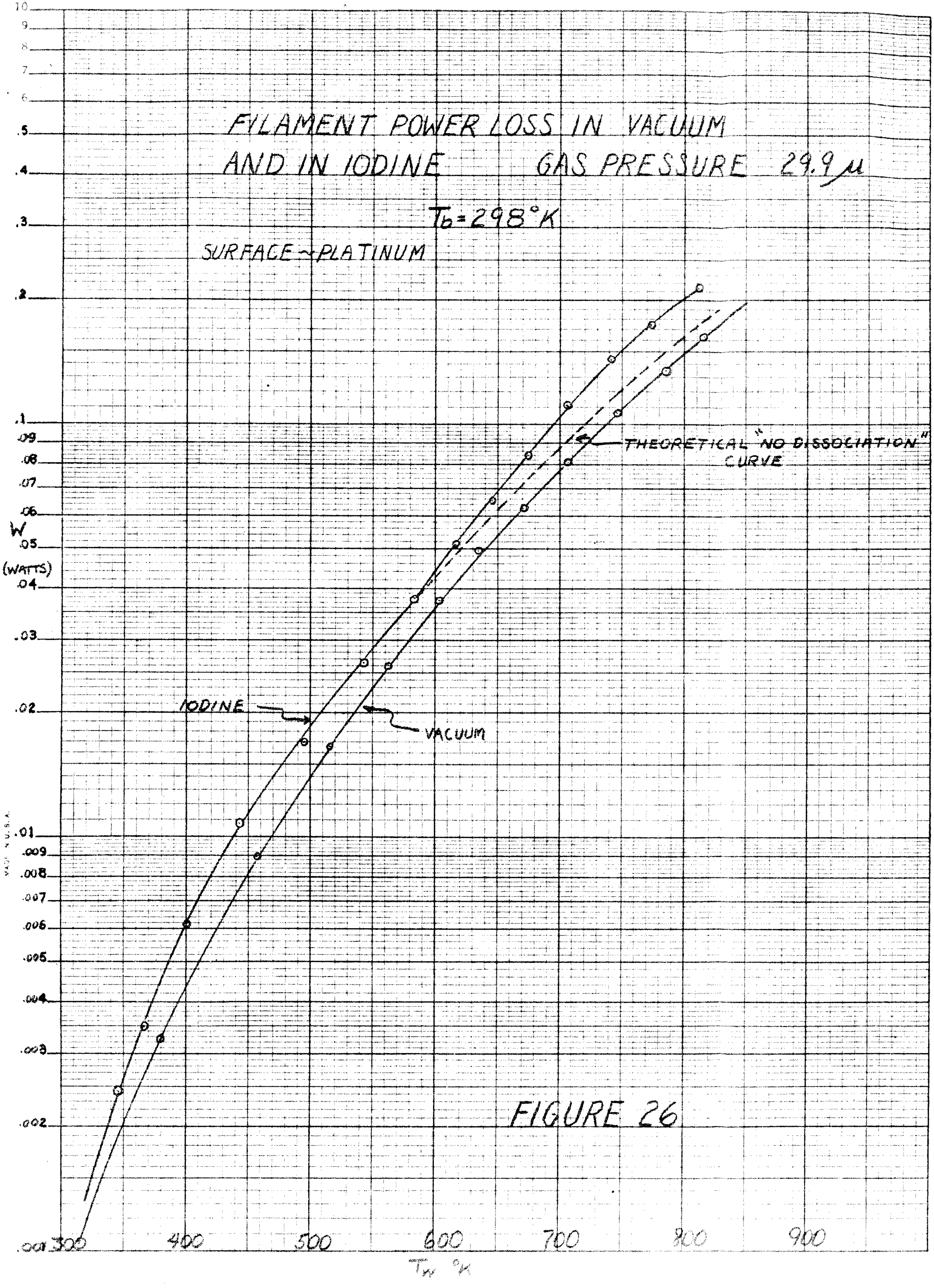
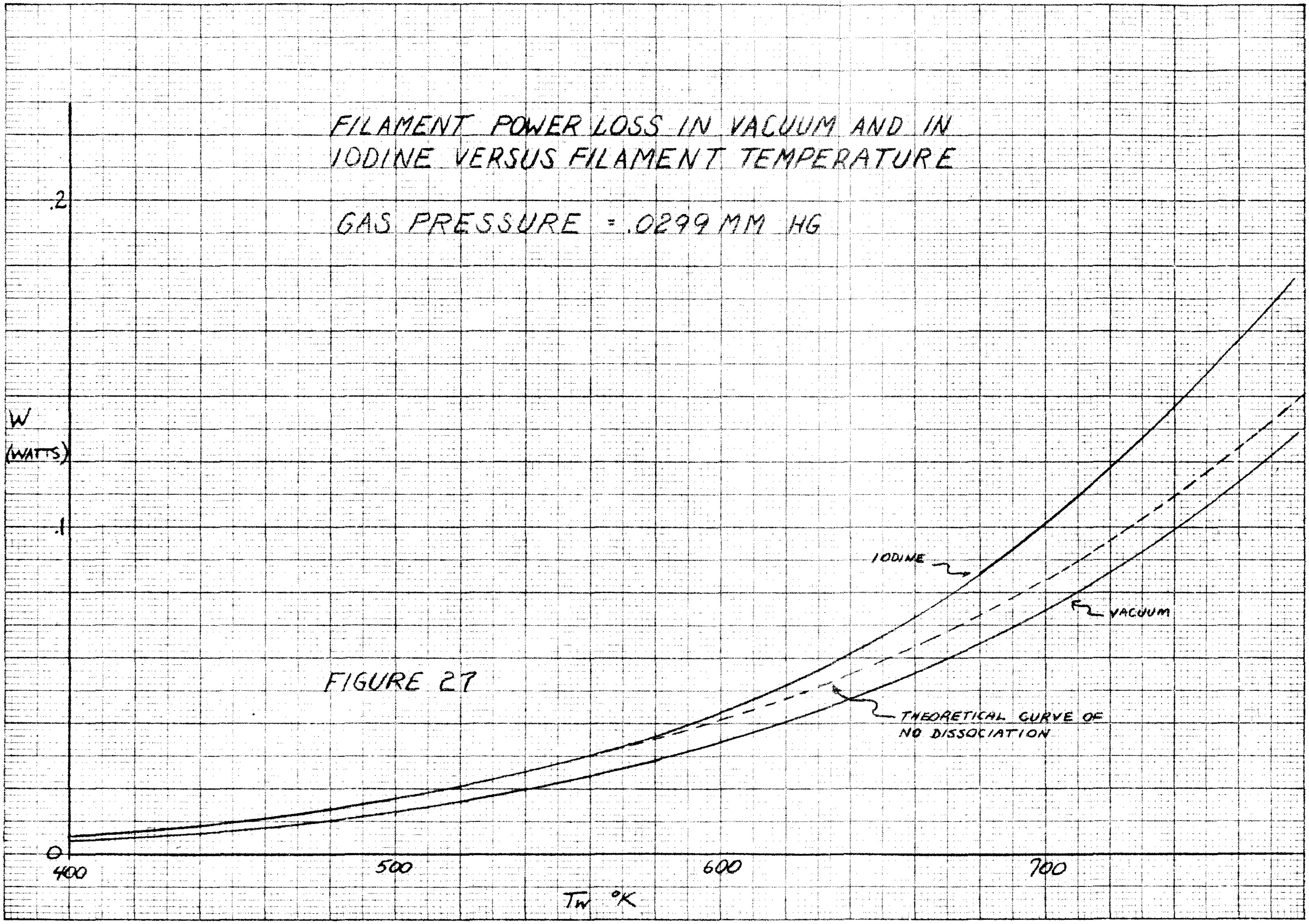

FILAMENT POWER LOSS IN VACUUM
AND IN IODINE GAS PRESSURE 29.9 μ
T_b=298°K
SURFACE ~ PLATINUM
THEORETICAL "NO DISSOCIATION" CURVE
IODINE
VACUUM
W (WATTS)
10
9
8
7
6
.5
.4
.3
.2
.1
.09
.08
.07
.06
.05
.04
.03
.02
.01
.009
.008
.007
.006
.005
.004
.003
.002
.001
300
400
500
600
700
800
900
T_W °K

FIGURE 26



FILAMENT POWER LOSS IN VACUUM AND IN IODINE VERSUS FILAMENT TEMPERATURE

GAS PRESSURE = .0299 MM HG

FIGURE 27

HEAT OF DISSOCIATION OF IODINE

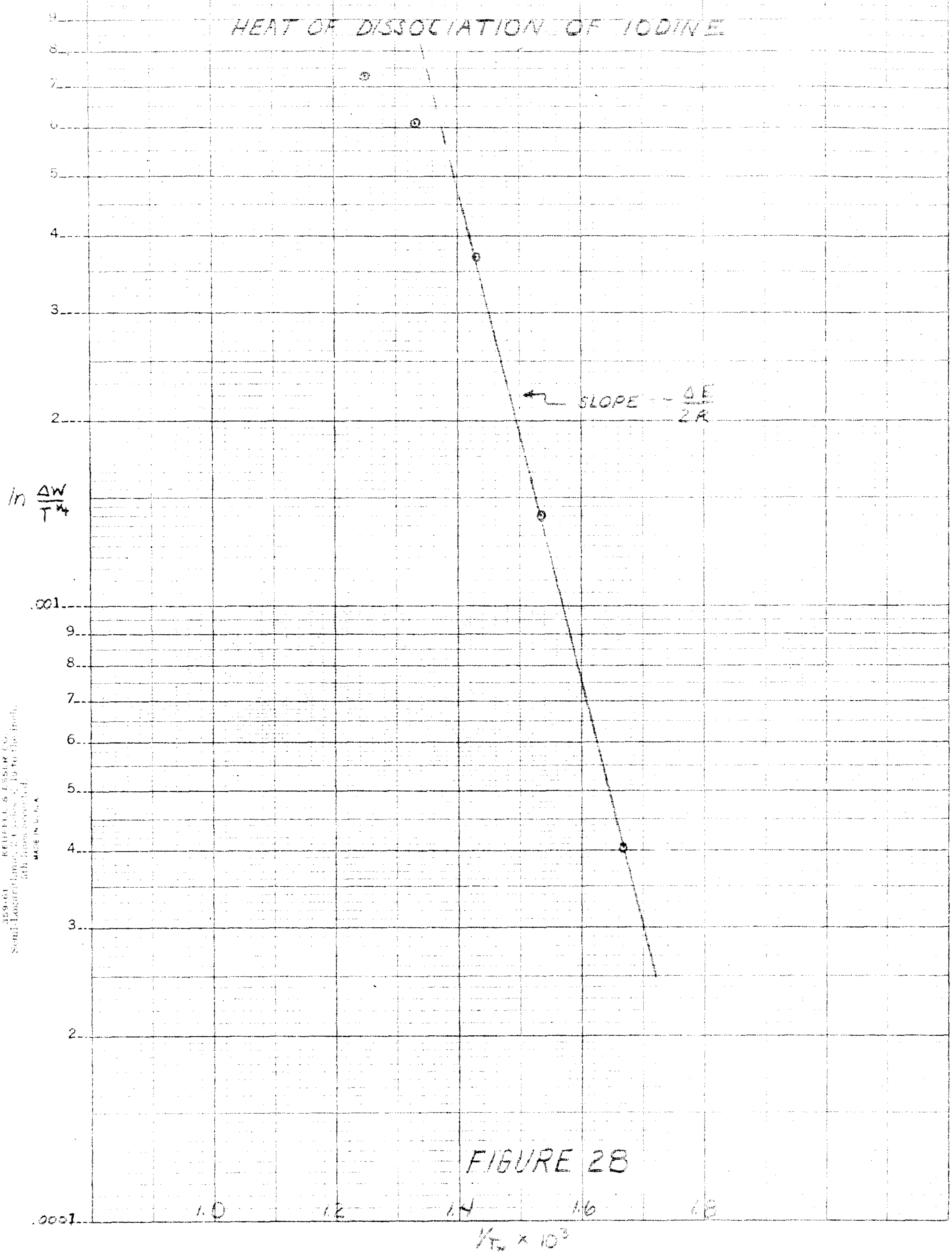


FIGURE 28