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April 12, 1963

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ABSTRACT

The exchange of energy between a tungsten filament heated at 1710° to 2500°K and cold helium, neon, argon, nitrogen, and carbon dioxide was studied at gas pressures from 0.1 to 10 μ Hg. The exchange of energy was found to be directly proportional to the gas pressure in the 1 to 10 μ range but essentially independent of the filament temperature. The results are interpreted in terms of a process in which the impinging gas molecules are first physically adsorbed, then heated until they gain sufficient thermal energy to overcome the attractive forces of the tungsten surface. On the average, the gas molecules then desorb at a critical temperature that is independent of the filament temperature. For the gases studied, the critical temperatures lie between 350° and 480°K. Reaction efficiencies of oxygen and carbon dioxide were calculated from the irreversible change in the rate of power consumption of the filament produced by introduction of these gases.

* This work was done under the auspices of the U.S. Atomic Energy Commission and is based on the M.S. thesis of Gerald L. De Poorter (UCRL-10504, November 12, 1962).

[†] University Fellow, 1961-62 academic year and Corning Research Foundation Fellow, 1962-63 academic year.

I. INTRODUCTION

Many studies have been reported of the transfer of thermal energy between surfaces and gases which were at temperatures only a few degrees different from the temperatures of the surfaces. There have been few studies, however, of the transfer of energy to cold gases from a solid held at much higher temperatures.

Meyer and Gomer investigated the energy increase imparted to several gases when a calculatable number of molecules of the gas underwent single collisions with the surface of a hot graphite filament.¹ They reached the important conclusion that the energy transferred per collision is independent of the temperature of the graphite provided that this temperature exceeds a rather low critical value. In this paper we report the results of a similar study of the transfer of energy from high-temperature tungsten filaments to cold gases.

The present work was undertaken for two reasons. First, the question of whether or not the energy exchange at a metal surface has the same surprising temperature independence found for graphite was of intrinsic theoretical interest. Second, knowledge of the efficiency of energy exchange between hot surfaces and cold gases should improve our understanding of the mechanism of reactions of gases with tungsten and other metals. In the several published studies of reaction of cold oxygen gas with tungsten filaments to yield volatile tungsten oxides, the assumption has been made that the cold oxygen has been readily adsorbed and efficiently heated to the temperature of the tungsten surface. The

¹L. Meyer and R. Gomer, J. Chem. Phys. 28, 617 (1958).

work of Meyer and Gomer suggests that, in fact, this process could be so inefficient as to constitute the rate-determining reaction step.

II. EXPERIMENTAL

A. Principle of the Experiment

The maximum possible rate of energy transfer to a cold gas from a hot surface is achieved if upon each collision of a gas molecule with the surface the molecule comes to complete thermal equilibrium with the surface. Blodgett and Langmuir give the following equation for the energy that is then carried away from the surface:²

$$W = \frac{p \int_{T_a}^{T_s} (\beta + 1/2) k dT}{(2\pi mkT)^{1/2}} = \frac{p(\beta + 1/2)k(T_s - T_a)}{\sqrt{2\pi mkT}^{1/2}} \quad (1)$$

where W = energy loss in $\text{erg/cm}^2\text{-sec}$, k = Boltzmann's constant, p = gas pressure in dyn/cm^2 , T_s = surface temperature, T_a = temperature of incident gas molecules, and βk = specific heat per molecule at constant volume.

When the reacting surface is a wire heated in a vessel of relatively large surface area and the pressure of the gas is low, the temperature of incident gas molecules is effectively the temperature of the vessel. All quantities needed for calculation of the theoretical rate of energy transfer are known or readily measured.

²K. Blodgett and I. Langmuir, *Phys. Rev.* 40, 78 (1932).

If the gas molecules do not reach thermal equilibrium before leaving the filament, the power loss per cm^2 is

$$W_c = \alpha W, \quad (2)$$

where α , the thermal-accommodation coefficients as defined by Knudsen,³ is the fraction of the theoretical rate of energy transfer that is actually achieved. And

$$\alpha = \frac{W_c (2 \pi m k T_a)^{1/2}}{p \int_{T_a}^{T_s} (\beta + 1/2) k dT} \quad (3)$$

or expressing W_c in watts/cm^2 and p in mm Hg, we have

$$\alpha = \frac{W_c (m)^{1/2}}{p \int_{T_a}^{T_s} (\beta + 1/2) k dT} \times 2.78 \times 10^{13} \quad (4)$$

In the present study, W_c was calculated from the change in power loss that resulted from introduction of a gas into the reaction vessel.

Filament temperatures between 1700° and 2500°K and vessel wall temperatures near 298°K were used. The interactions of the tungsten surface with helium, neon, argon, nitrogen, carbon dioxide, and oxygen were studied at 0.1 to 10μ pressure.

³S. Dushman, Vacuum Technique, 2nd ed. (John Wiley and Sons, Inc., New York, 1961), p. 46.

III. EXPERIMENTAL METHODS

A. Apparatus and Materials

The vacuum system consisted of a stainless steel reaction vessel, two cold traps, and a pumping system. A glass storage bulb of 2 liters capacity was connected to the reaction vessel by copper tubing. The bulb was also connected to the mechanical pump by a series of valves. A needle valve controlled the rate of flow of the gas into the reaction vessel. A small turret at the top of the gas inlet tube in the reaction vessel forced the gas stream to scatter so that the directions of movement of molecules that struck the filament would be random. A complete description of the system is given by Anderson.⁴

The lines and glass bulb are evacuated and flushed several times with the gas under study before each experiment. Each gas is introduced through a liquid nitrogen cold trap.

The pressure in the reaction vessel was measured with a hot-filament ion gauge which was connected by a short 1 in. diam tube to the side wall of the reaction vessel. The gauge was a Veeco Type RG 21A with an RG 76K ionization tube. The pressure during the energy-exchange experiments was measured with an Alpatron Type-530 vacuum gauge that was connected at the same point as the ionization gauge. The calibration of the Alpatron gauge was checked against a McLeod gauge.

The tungsten filament was suspended as a loop, 47 cm long and 0.0127 cm in diam, from the top of the reaction vessel. The filament

⁴H. U. Anderson, "Kinetic Studies of Reactions Occurring Between Tungsten and Gases at Low Temperatures and High Pressures" (Ph. D. Thesis), Lawrence Radiation Laboratory Report UCRL-10135, April 1962 (unpublished).

was held in molybdenum holders which were connected to copper rods that passed out of the reaction vessel through a kovar glass seal. The temperature of the filament was determined from its electrical properties as reported by Langmuir.⁵ Corrections in surface area for end effects were made as described by Forsythe and Worthing.⁶

The electric power Q required to heat the filament is given by $Q = EI$, where I is the current and E the voltage; therefore, at constant E , $dQ = EdI$. From the voltage across the filament and the change in current caused by the energy exchange, the power loss to the gas can be determined. Since the maximum temperature drop of the filament was only a few tenths of a degree, the power changes caused by changes in radiation were negligible.

Twelve 6-volt storage batteries were used as a power source to heat the filament. The filament current was determined by measuring the potential drop across a $1-\Omega$ standard resistor connected in the positive side of the line. The standard resistor was wound from Nichrome wire and was placed in a constant-temperature oil bath. A Hewlett-Packard Model 425A μ V ammeter was employed as a dc amplifier. An amplification factor of 10 was usually used. The amplifier output was recorded on a Varian G-10 Graphic Recorder.

The tungsten was supplied by the Thermionic Products Company and was 99.95% pure. The gases were analyzed with a mass spectrometer

⁵H. A. Jones and I. Langmuir, Gen. Elec. Rev. 30, 310 (1927).

⁶W. E. Forsythe and A. G. Worthing, Astrophys. J. 61, 146 (1925).

connected directly into the system. Unfortunately, the mass spectrometer had a very high water background so the gases could not be analyzed for water content. Because there was a liquid nitrogen cold trap between the mass spectrometer and the reaction vessel as well as between the storage vessel and the reaction vessel, the water background in the reaction vessel is believed to be low. No other impurities were detected in the gases.

B. Experimental Procedure

After a filament is placed in the reaction vessel, the system is evacuated. The reaction vessel is outgassed and the second cold trap is filled. The filament is then aged by heating to 2600°K for approximately 48 hours. This procedure has been demonstrated to drastically lower the carbon content in the tungsten.⁴ The background pressure in the reaction vessel is between 4 and 6×10^{-6} mm Hg.

The filament is heated. The heater and circulating pump in the oil bath are turned on. After 15 to 30 min the standard resistor comes into thermal equilibrium with the oil bath and the current becomes stable.

An energy exchange determination is made as follows: With the amplifier and recorder on, the filament current is monitored. Gas is admitted to the reaction vessel through the needle valve. The gas pressure is noted and the current change is recorded. The needle valve is closed and the gas is pumped out. The system is allowed to pump for 5 to 10 min before another determination is made.

The shape of the energy-transfer curves gave evidence that reactive impurities were not present at significant concentrations in the inert gases tested. The filament current was very sensitive to small

changes in filament diameter caused by reaction of gases with the filament. When oxygen was introduced at even 0.1μ pressure, for example, the electric current flow decreased continuously as long as the gas flow persisted. Upon termination of the oxygen flow, the current flow did not increase again. Introduction of any of the nonreactive gases caused a current increase and upon termination of the gas flow, the current flow returned to the same level that had been established before the gas was introduced. The reversibility of this process constitutes good evidence that gaseous impurities did not produce the effects that we have attributed to the gases deliberately introduced.

IV. RESULTS AND DISCUSSION

With the apparatus of this research, energy exchange measurements were made with pressures as low as 0.1μ compared to about 6μ for the lower limit in the study of Meyer and Gomer.¹

The results of the energy-exchange experiments for neon, argon, nitrogen, and carbon dioxide are shown graphically in Figs. 1 to 4 which are plots of energy loss per unit area of filament against gas pressure. The energy losses were calculated by use of the equation $dQ = EdI$.

Experiments with helium were performed only at 1870°K because the Alpatron vacuum gauge did not work well for helium. For helium, the gauge response was very slow and the indicator fluctuated badly.

The extrapolation of the power loss curves to zero pressure do not pass exactly through the origin. The pressure read at the Alpatron gauge, which is connected into a side arm of the reaction vessel, cannot be identical with the pressure in the reaction vessel. Probably the

pressure read on the Alphasatron is slightly lower than the pressure in the reaction vessel.

Since the curves of power loss vs pressure do not go through the origin, values of W_c/p in Eq. (4) were obtained from the slopes of the power loss vs pressure curves to calculate the thermal-accommodation coefficient for the gases in the 1 to 10μ pressure range. In this pressure range these slopes are constant with pressure and are nearly independent of temperature. Calculations of thermal-accommodation coefficients α from the data are summarized in Table I.

The thermal-accommodation coefficient can be looked on as a measure of the extent to which the impinging gas achieves temperature equilibrium with the surface. Thus, $\alpha = (T_c - T_1)/(T_2 - T_1)$, where T_1 is the temperature of the incident gas molecules, T_2 is the filament temperature, and T_c is the average temperature of the gas molecules when they leave the filament. Values for T_c for helium, neon, and argon calculated from this equation are given in the last column of Table I. For nitrogen and carbon dioxide, T_c is calculated from the expression

$$W_c = (3.37 \times 10^{-3}) \frac{p}{(M)^{1/2}} \int_{T_1}^{T_c} (C_v + R/2) dT.$$

Values of T_c for nitrogen and carbon dioxide are also given in Table I.

Meyer and Gomer argued that the attractive forces between a graphite surface and the inert gases should be of the van der Waals type and that as a result the thermal-accommodation coefficients should vary with the square root of the van der Waals constant a . The thermal-accommodation coefficients showed the predicted trends from gas to gas.

Table I. Results of Energy-Exchange Experiments

Gas	Temperature (°K)	$\frac{d(dQ)}{d \text{ Pressure}}$ (W/ μ)	Accommodation coefficient	Accommodation coefficient (from av slope)	T _c (°K)
Neon	1710	1.80	0.0452	--	364
Neon	1880	2.43	0.0545	0.0549	386
Neon	1986	2.48	0.0521	0.0514	387
Neon	2120	2.44	0.0475	0.0476	386
Neon	2350	1.665	0.0289	--	359
Average from 1880° to 2130°K	--	2.45	--	--	386
Argon	1860	1.00	0.0865	0.091	435
Argon	2120	1.15	0.0854	0.078	465
Argon	2240	1.05	0.073	0.073	442
Argon	2335	1.00	0.0664	0.0698	435
Average	--	1.05	--	--	442
Nitrogen	1870	2.26	0.076	0.083	435
Nitrogen	2120	2.50	0.071	0.070	449
Nitrogen	2240	2.60	0.069	0.0655	455
Nitrogen	2335	2.50	0.063	0.062	449
Nitrogen	2425	2.49	0.060	0.059	449
Nitrogen	2511	2.45	0.0565	0.057	446
Average	--	2.466	--	--	445
Carbon dioxide	1860	1.975	0.087	--	467
Carbon dioxide	2120	2.15	0.073	--	481
Helium	1870	1.575	0.0359	--	356

The forces between a tungsten surface and the impinging gas molecules are not of the van der Waals type. Van der Waals forces are induced dipole-induced dipole interactions. The oxygen atoms on the tungsten surface are certainly polarized so that the forces between the surface and the gases are dipole-induced dipole interactions. Nevertheless, the interaction of nonreacting gases with tungsten can be interpreted in an analogous manner to that for carbon. The T_c calculated from the accommodation coefficients for each gas were constant as shown in Table I.

The inert gases cannot displace chemisorbed oxygen so that we must interpret our data as characteristic of interaction of the gases with a tungsten surface covered by whatever concentration of oxygen (and nitrogen) was established by the background pressure of our apparatus at the temperature of the experiment. According to Becker, Becker, and Brandes⁷ for the background pressures of 4 to 6 x 10⁻⁶ mm characteristic of our apparatus, the tungsten surface should be covered by from .01 to 1.01 layers of adsorbed oxygen with the highest coverage, of course, at the lowest temperatures. It is interesting that for the nonreacting gases the critical temperature calculated for desorption was independent of whether a complete layer of oxygen was present or whether only a small fraction of a layer was present.

The energy per collision for the rare gases varies approximately with the van der Waals a value as found by Meyer and Gomer for graphite interactions (Fig. 5). At a constant temperature and pressure, the energy

⁷J.A. Becker, E.J. Becker, and R.G. Brandes, J. Appl. Phys. 32, 411 (1961).

exchange per unit time depends on the velocity of the gas molecules as well as on the thermal-accommodation coefficient and heat capacity of the gas. The rate of energy-exchange for helium is higher than for neon and argon despite the low accommodation coefficient of helium because of the high velocity of the helium atom.

The energy-exchange curves for nitrogen and carbon dioxide lie above those for the inert gases for two reasons. Nitrogen and carbon dioxide have higher values of T_c and in addition have higher heat capacities because rotational and vibrational modes must be excited to raise their temperatures.

Energy exchange between oxygen and the tungsten filament proved impossible to measure because the reduction of the filament cross section produced by the tungsten-oxygen reaction caused a change in the power loss that masked any cooling effects. The current decreased continuously as long as oxygen was introduced. The rate of tungsten loss was calculated from the power change by means of the expression

$$R_w = \frac{2 \pi N_o \rho d^4 dI}{M I^2 R^1}$$

where

N_o = Avogadro's N_o

d = filament diameter

ρ = density of W

M = molecular weight of W

I = filament current

dI = current change caused by reaction

R^1 = characteristic electrical property of W.

Application of this equation at 1855°K and $P_{O_2} = 2.1 \times 10^{-7}$ atm yields $R_w = 3.1 \times 10^{15}$ atoms/sec/cm² compared to $R_w = 0.832 \times 10^{15}$ obtained by Anderson.⁴ From our value the efficiency of an oxygen molecule collision in producing $W(s) + O_2(g) = WO_2(g)$ is calculated to be 0.064.

Energy-exchange experiments with carbon dioxide when performed at 1860°K yielded results similar to those for nonreactive gases. At 2120°K, reaction between carbon dioxide and tungsten was noticeable. The current decreased slowly and irreversibly after an initial reversible increase (Fig. 6). This behavior must arise because of superposition upon the normal cooling effect produced by nonreactive gas molecules of an irreversible reaction of a small fraction of the carbon dioxide molecules with the tungsten which reduces the filament diameter. For the reaction at 2120°K and $P_{CO_2} = 2.8 \times 10^{-7}$ atm, $R_w = 1.9 \times 10^{13}$ and the efficiency of reaction per CO_2 collision is calculated to be 1.45×10^{-4} .

Even at 1860°K a large fraction of CO_2 would react with the tungsten if equilibrium were established. The fact that reaction is observed at 2120°K and not at 1860°K must be attributed to a kinetic factor. Perhaps the important difference is that the reduced concentration of oxygen on the surface increases the probability of chemisorption of CO_2 on the tungsten.

The most striking result of our research is the contrast that it reveals between the behavior of cold oxygen on striking a hot surface and the behavior of the other gases studied. If the oxygen molecules could all revaporize upon reaching a critical temperature comparable to the low critical temperatures of the other gases studied, no measurable rate of reaction would be expected. We can estimate an expected critical

temperature for O_2 from comparison of the van der Waals a value for O_2 with that for N_2 . We expect that $T_c(O_2) \cong T_c(N_2) [a(O_2)]^{1/2} / [a(N_2)]^{1/2} \cong 440^\circ K$. Whereas N_2 molecules cannot become chemisorbed without overcoming an energy barrier that exceeds $2RT_c = 1750$ cal/mole, the energy barrier for chemisorption of O_2 must be lower than $2R \times 440 = 1700$ cal/mole. An incoming O_2 molecule must be attracted by the energy field of the surface much more strongly than is nitrogen. The polarizabilities of O_2 and N_2 molecules are nearly the same. The greater attraction of a tungsten surface for oxygen may be related to the presence of two unpaired electrons on an oxygen molecule that are absent on a nitrogen molecule.

Experiments on the energy exchange of a tungsten surface with F_2 molecules should be of special interest because the F_2 molecule has no unpaired electrons, but is much more polarizable than is O_2 . We hope to examine the energy exchange between hot tungsten surfaces and F_2 , as well as other halogen molecules, in a future investigation.

LEGEND OF FIGURES

- FIG. 1 Power loss vs neon pressure;
actual pressure = $2.28 \times$ gauge pressure.
- FIG. 2 Power loss vs argon pressure;
actual pressure = $0.840 \times$ gauge pressure.
- FIG. 3 Power loss vs nitrogen pressure;
actual pressure = $1.04 \times$ gauge pressure.
- FIG. 4 Power loss vs carbon dioxide pressure;
actual pressure = $0.633 \times$ gauge pressure.
- FIG. 5 Power loss per collision.
- FIG. 6 Sketch of recorder trace for carbon dioxide.

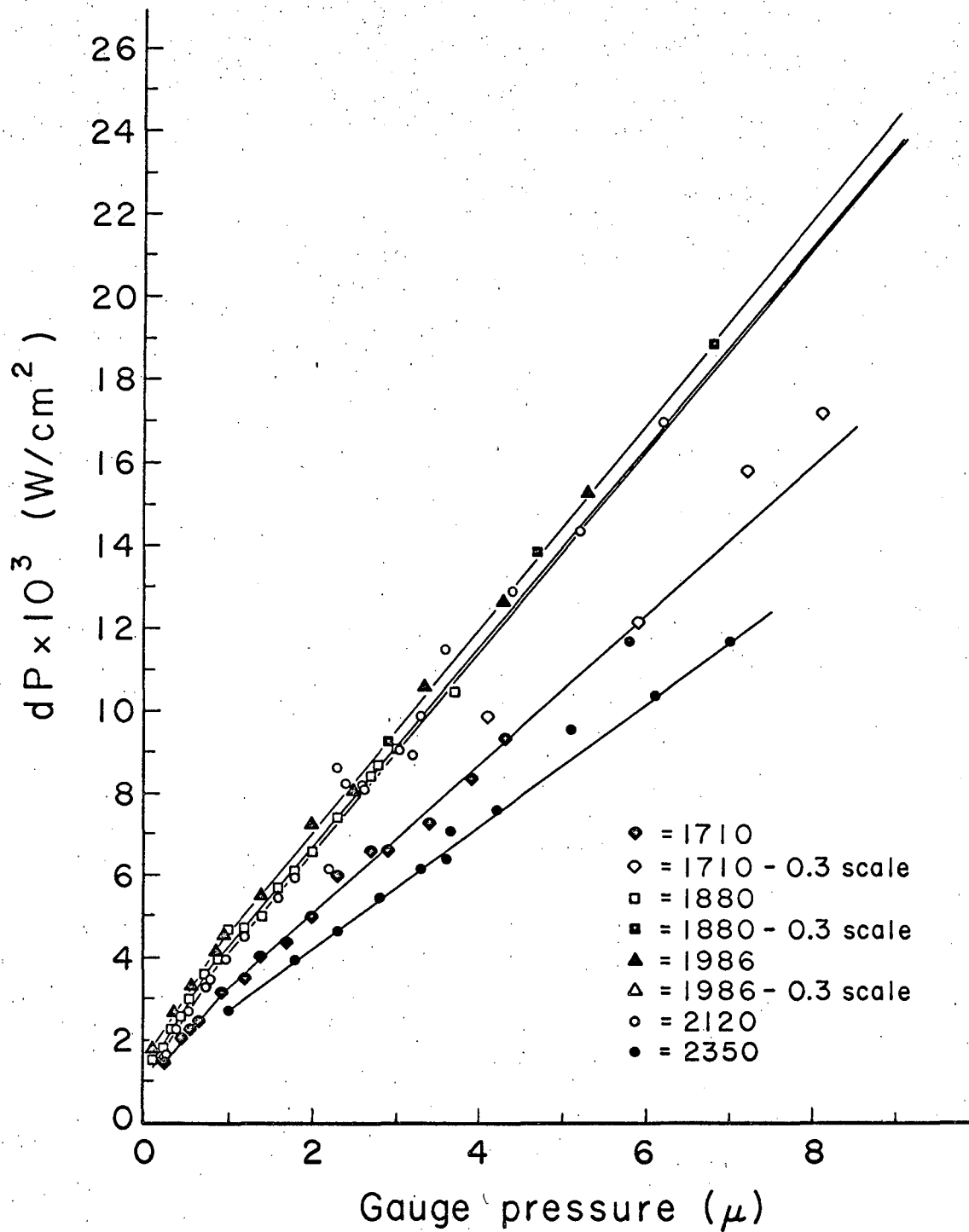
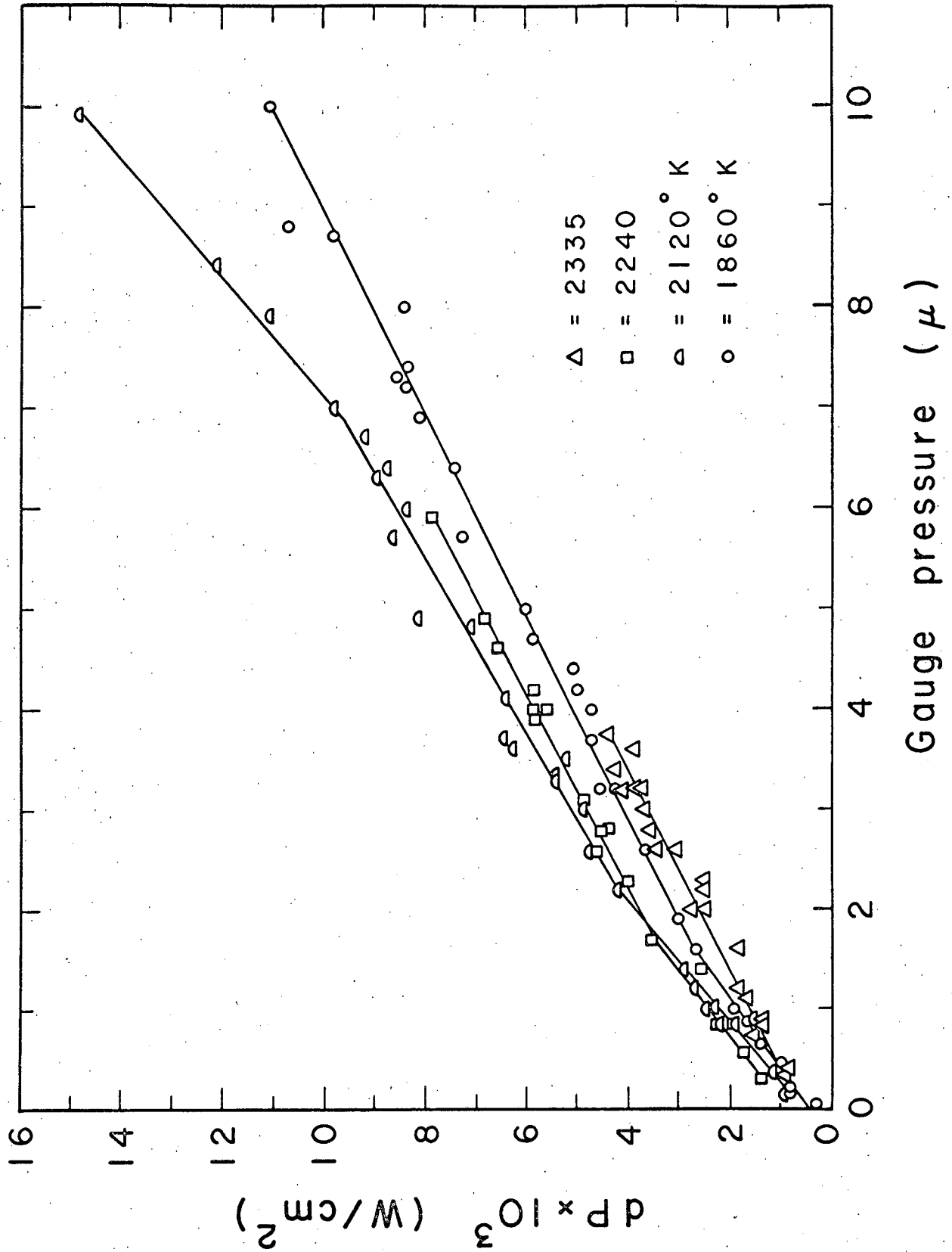


Fig. 1.

MUB-1552



MU-29011

Fig. 2.

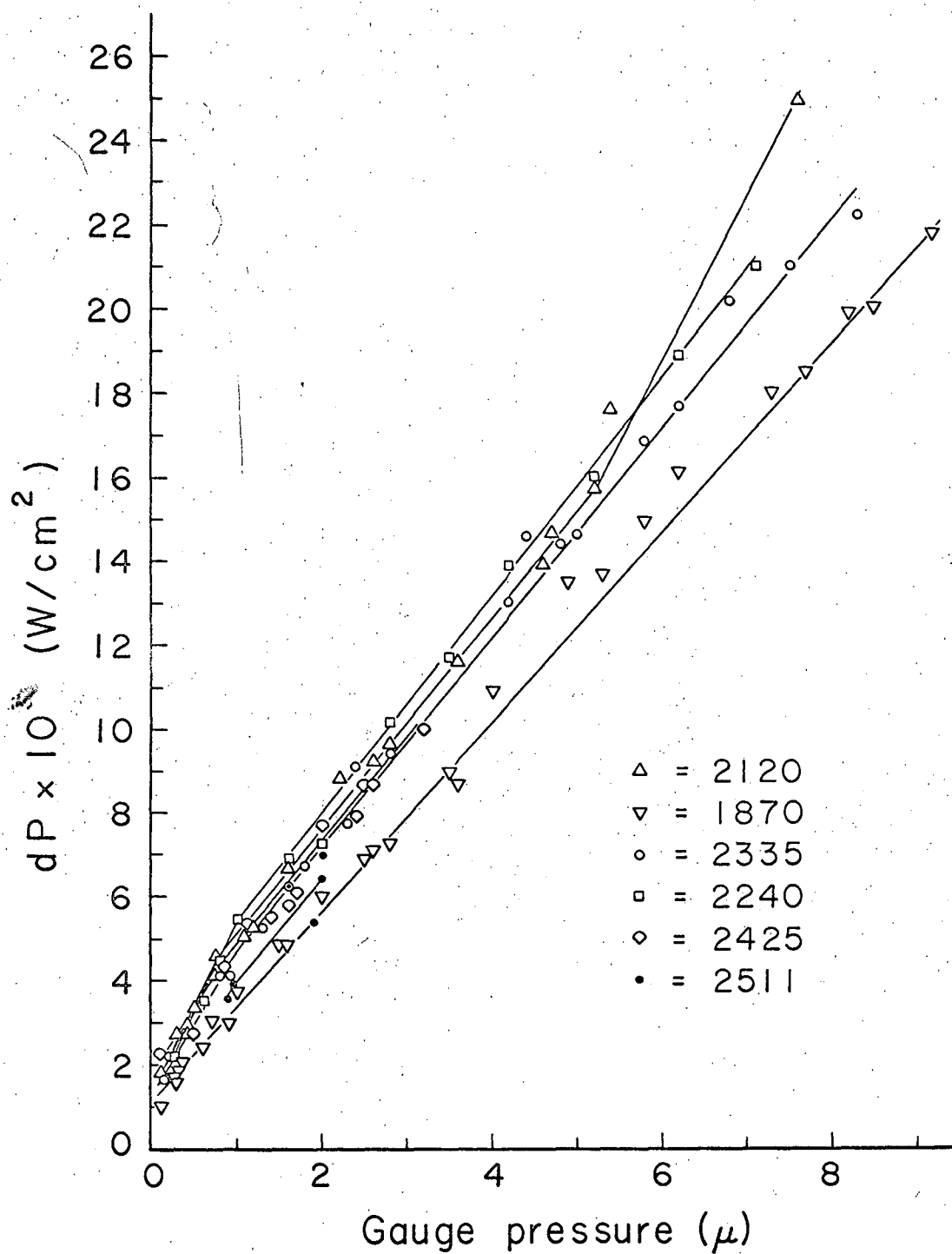
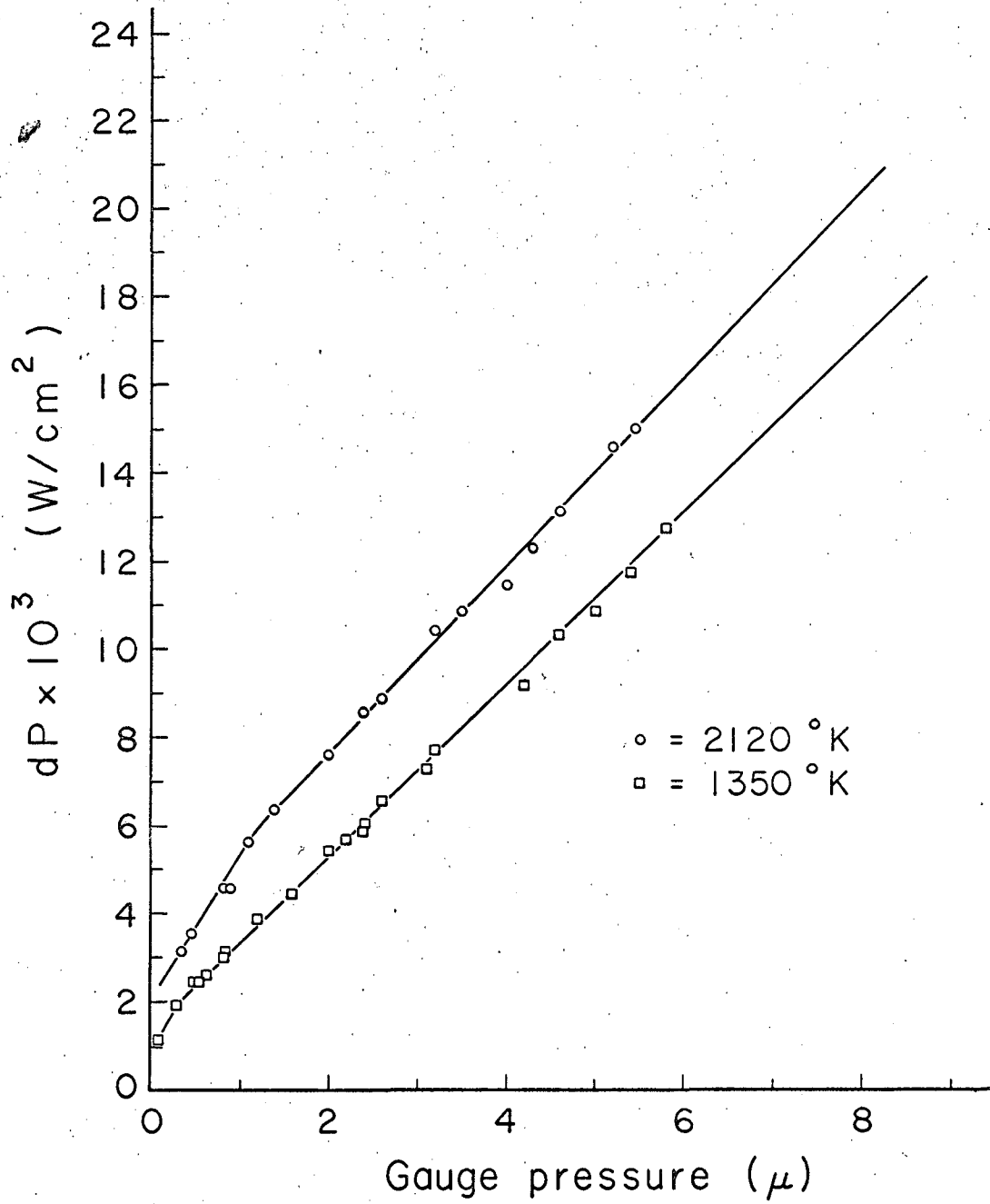


Fig. 3.

MUB-1553



○ = 2120 °K
□ = 1350 °K

Fig. 4.

MUB-1554

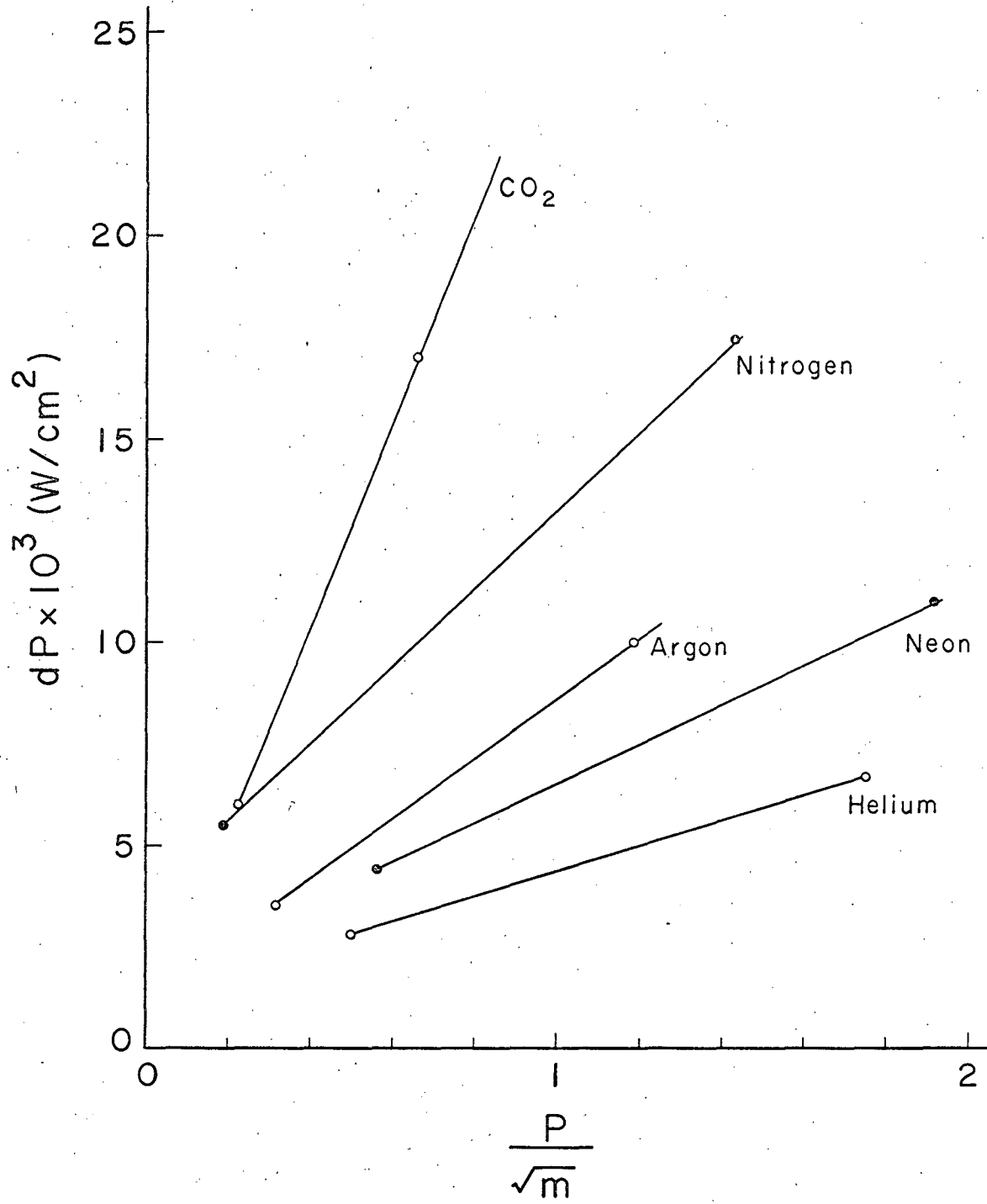


Fig. 5.

MUB-1556

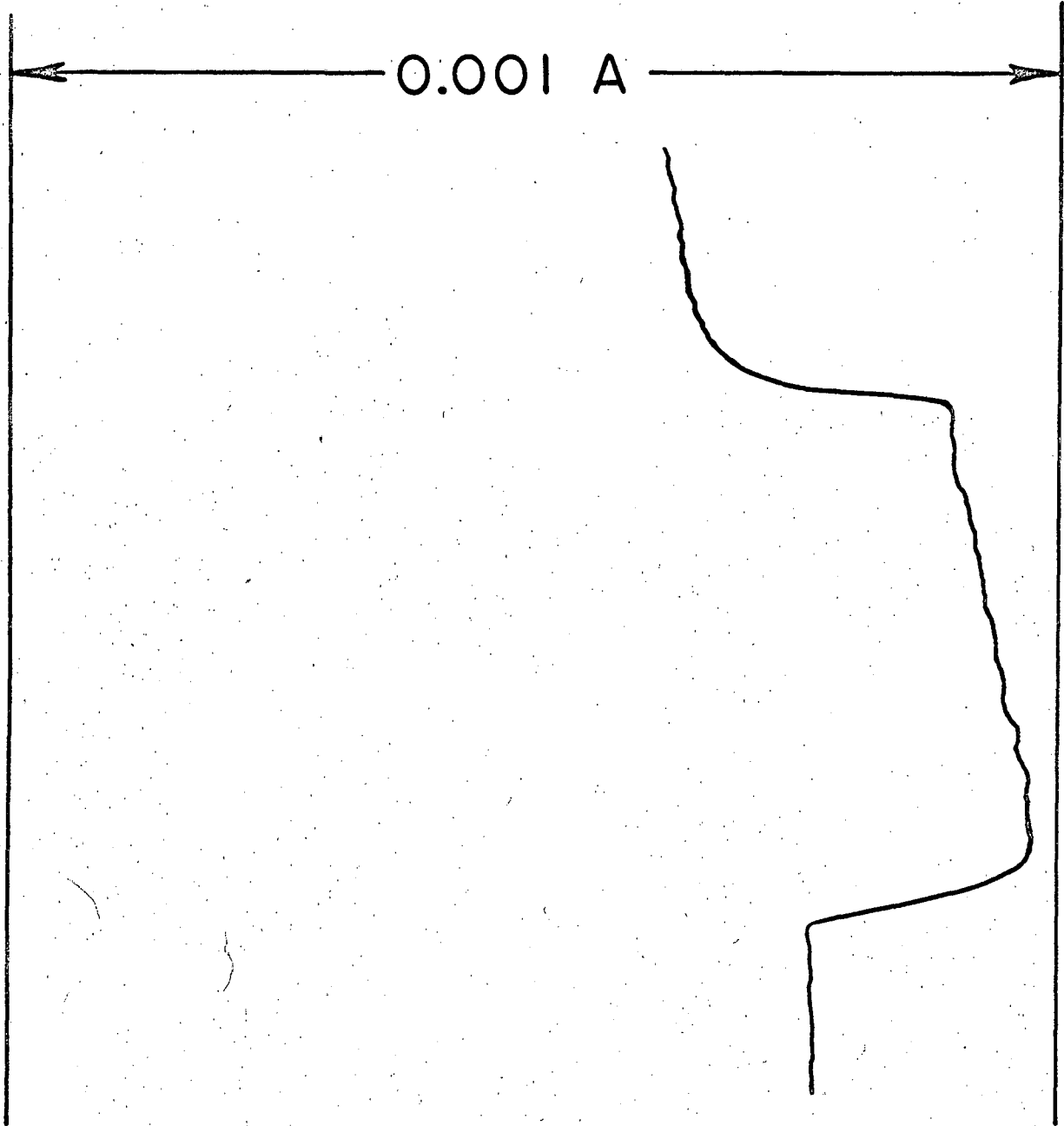


Fig. 6.

MU-29014

