Title

ENERGY EXCHANGE BETWEEN COLD GASE MOLECULES AND A HOT TUNGSTEN SURFACE

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Publication Date

1962-11-12

Thesis/dissertation

UCRL-10504

University of California

Ernest O. Lawrence Radiation Laboratory

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(M.S. Thesis)

November 12, 1962

Printed in USA. Price 75 cents. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D.C.

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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 is studied. Gas pressures from 0.1 to 10μ Hg are used. The exchange of energy is directly proportional to the gas pressure but is 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 certain "critical" temperature that is independent of the filament temperature. The critical temperatures for the gases used lie between 350° and 550°K.

INTRODUCTION

Most kinetic studies of gas-solid reactions at high temperatures and low pressures are conducted with only the solid directly heated and with the bulk of the gas at room temperature. This procedure is adopted because of the experimental difficulty of heating the gas. Unfortunately, the usual assumption that the effective temperature of reaction is that of the solid may be incorrect. The effective temperature of the gas when it reacts with the solid is unknown. Also unknown is the fraction of gas molecules that may revaporize from the surface before reaching a temperature high enough to permit reaction.

Studies of the energy exchange between hot metals and cold, nonreactive gases may reduce the uncertainty on these points by establishing the average energy per molecule--and thus the average effective temperature--acquired before the molecules revaporize.

Most of the reported work on energy exchange between gas atoms and solid surfaces has been performed with a small temperature gradient between the solid and the gas. Roberts, for example, has measured the thermal accommodation coefficient of helium on clean nickel and tungsten surfaces.[1] The metal filaments were heated no more than 10 to 30° above the temperature of the surroundings. The accommodation coefficients measured showed no dependence on the gas pressure over the range 0.044 to 0.14 mm Hg. For helium on tungsten the thermal accommodation coefficient α was between 0.05 and 0.07, and for helium on nickel α was 0.085: both values were for a surface cleaned of adsorbed gases by heating to 2000°C.

Roberts also studied the temperature variation of the accommodation coefficient of helium and neon on tungsten.[2, 3] A summary of his results is given in Table I.

Table I. Temperature variation of the accommodation coefficient of helium and neon on tungsten.[2, 3]

Temperature (°K)	α neon	α helium
295	0.07	0.057
195	0.08	0.046
79	0.08	0.025

More recent values for the thermal-accommodation coefficients of helium and neon on tungsten are given as 0.017 and 0.042, respectively, by Wachman.[4] According to Wachman these values are among the most reliable available. For argon on clean tungsten, Thomas reports a value of 0.271 for the accommodation coefficient at 30° C, and 0.294 at -30°C.[5]

Meyer and Gomer appear to be the only investigators to have reported a study of the energy exchange cold gases and a hot surface.[6,7] Their results showed that Q, the heat loss from a graphite filament, varied linearly with gas pressure up to 15μ and that Q depended very little on the filament temperature between 850° and 1500° C for all the gases investigated.

Meyer and Gomer concluded that gas molecules that impinge on the hot surface are first adsorbed, then heated until they gain sufficient thermal energy to overcome the van de Waals forces of the graphite surface. The gas molecules then desorb at a certain "critical" temperature T_c. As long as the filament temperature T_f is higher than T_c, the amount of energy carried away from the filament by the gas molecules is essentially independent of T_f and is determined by T_c.

A most interesting finding was that methane did not pyrolize upon collision with graphite filaments heated to 2300° C unless the filaments had been activated or contaminated, presumably because the critical temperature for desorption lay below the temperature necessary for reaction.

The object of the present investigation was to study the energy exchange between cold gas molecules and a hot tungsten surface. The average temperature reached by the gas molecules before revaporization was calculated from measurements of energy exchanged.

PRINCIPLE OF THE EXPERIMENT

Blodgett and Langmuir give the following equation for the energy that is carried away from a filament if the impinging gas molecules reach thermal equilibrium before leaving the filament:[8]

$$W = \frac{(\beta + \frac{1}{2})\, kp(T - T_a)}{(2\pi mkT_a)^{1/2}} \qquad (1)$$

where

W = energy loss in erg/cm^2-sec,
k = Boltzman constant,
p = gas pressure in dyn/cm^2,
T = filament temperature,
T_a = temperature of incident gas molecules,

and βk = specific heat at constant volume per molecule.

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

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

where α is the thermal-accommodation coefficients as defined by Knudsen.[9] Therefore we have

$$\alpha = \frac{W_c(2\pi mkT_a)^{1/2}}{(\beta+\frac{1}{2})kp(T - T_a)} . \qquad (3)$$

Expressing W_c in W/cm^2 and p in mm Hg, we have

$$\alpha = \frac{W_c(m)^{1/2}}{(\beta+\frac{1}{2})p(T - T_a)} \times 2.78 \times 10^{13}. \qquad (4)$$

From measurements of the power loss per unit area of the filament the thermal-accommodation coefficient can be calculated.

Filament temperatures between 1700° and 2500° K were used for this investigation. The interaction of the tungsten surface with helium, neon, argon, nitrogen, carbon dioxide, and oxygen were studied at 0.1 to 10μ pressure.

EXPERIMENTAL METHODS

Description of Apparatus

The vacuum system consists of a stainless steel reaction vessel, two cold traps, and a pumping system. The schematic diagram in Fig. 1 illustrates the arrangement of the components. A complete description of the vacuum system is given by Anderson.[10]

The gas container is a glass bulb of 2 liters capacity connected to the reaction vessel by copper tubing. The bulb is also connected to the mechanical pump by a series of valves. A needle valve controls the flow rate of the gas into the reaction vessel. A small turret at the top of the gas inlet tube in the reaction vessel forces the gas molecules to strike the reaction-vessel wall before striking the filament.

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 background pressure in the reaction vessel is measured with a hot-filament ion gauge. The gauge is a Veeco Type RG 21A with a RG 76K ionization tube.

The pressure during the energy-exchange experiments is measured with an Alphatron Type-530 vacuum gauge. The calibration of the Alphatron gauge was checked against a McLeod gauge. The location of the pressure gauges is shown in Fig. 1 (sketch of apparatus).

The tungsten under study is a filament about 47 cm long and 0.0127 cm diam. The filament is suspended as a loop from the top of the reaction vessel. The filament is held in molybdenum holders which are connected to copper rods that pass out of the reaction vessel through a kovar glass seal.

The temperature of the tungsten filament is determined from its electrical properties as reported by Langmuir.[11]

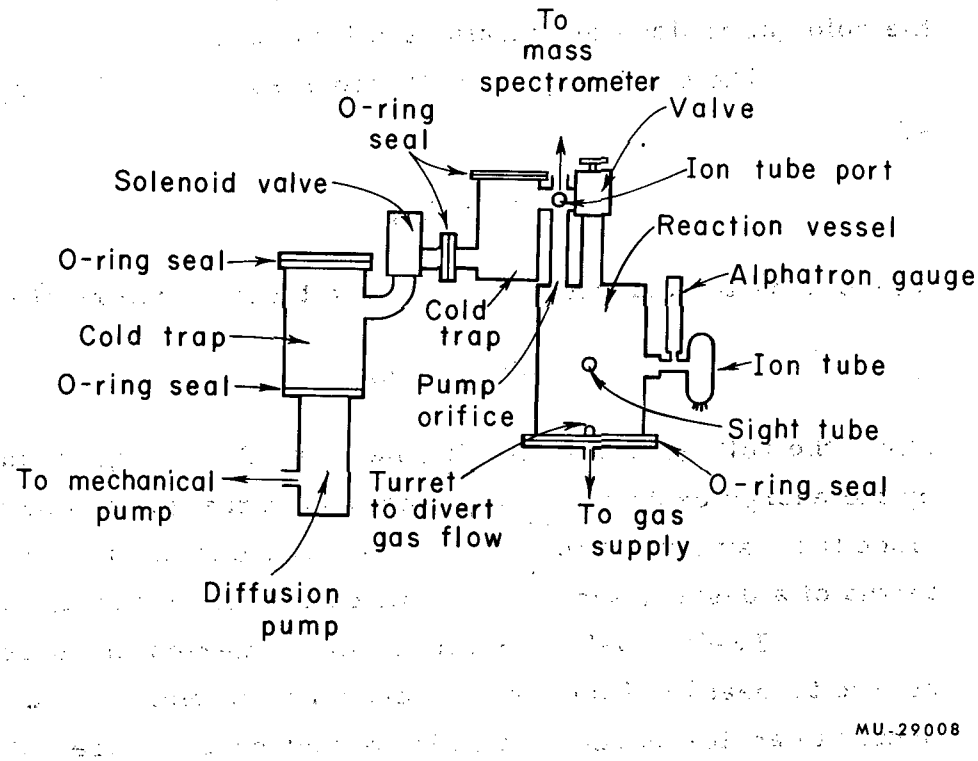

Fig. 1. Schematic diagram of the apparatus.

Since the diameter of the filament does not change during the energy-exchange experiments, the function $I/d^{3/2}$ is used to determine the filament temperature. This relationship gives the true temperature of the constant-temperature section of the filament regardless of any end effects. Corrections in surface area for end effects are made as described by Forsythe and Worthing.[12]

The energy exchange between the gas molecules and the tungsten surface is determined by measuring the current change caused by the cold gas molecules striking the filament.

The electric power Q required to heat the filament is given by

$$Q = EI, \tag{5}$$

where I is the current and E the voltage; therefore at constant E

$$dQ = EdI. \tag{6}$$

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 is only a few tenths of a degree, the power changes caused by radiation are negligible.

Twelve 6-V 145-Ah storage batteries are used as a power source to heat the filament. Whenever possible, the batteries are connected in series-parallel in order to reduce the current drain. A cable runs directly from the batteries to the filament. Between the batteries and the filament there are no switches and no variable resistances.

The filament current is determined by measuring the potential drop across a 1-Ω standard resistor placed in the positive side of the line. The standard resistor is wound from Nichrome wire and is placed in a constant-temperature oil bath.

Figure 2 is a schematic diagram of the electrical measuring system. A Hewlett-Packard Model 425A μV ammeter is used as a dc amplifier. An amplification factor of 10 is primarily used. The amplifier output is recorded on a Varian G-10 Graphic Recorder.

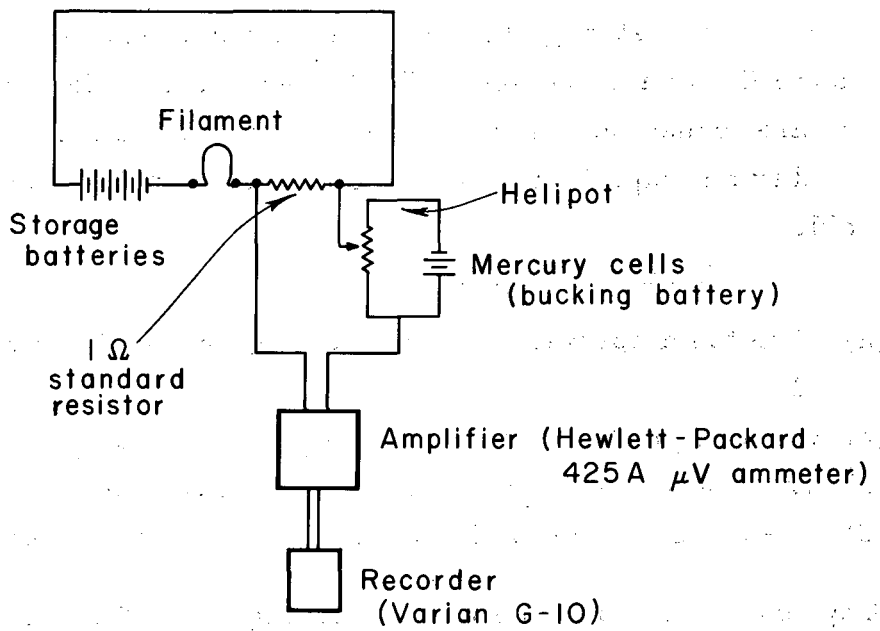

Fig. 2. Electrical measuring circuit.

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 $2600^{\circ}K$ for approximately 48 hours. The background pressure in the reaction vessel is between 4 and 6×10^{-6} mm Hg.

The storage batteries are wired to give the desired voltage, and 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.

A run is made as follows:

(a) With the amplifier and recorder on, the filament current is monitored.
(b) Gas is admitted to the reaction vessel through the needle valve.
(c) The gas pressure is noted and the current change is recorded.
(d) The needle valve is closed and the gas pumped out.

A typical recorder trace is given in Fig. 3. The system is allowed to pump for 5 to 10 min before another run is made.

Materials Used

The tungsten was supplied by the Thermionic Products Company and was 99.95% pure.

The gases were analyzed with a mass spectrometer connected directly into the system. Unfortunately the mass spectrometer had a very high water background. Thus, the gases used could not be analyzed for water content. Because there was a liquid nitrogen cold trap between the mass spectrometer and the reaction vessel the water background in the reaction vessel is believed to be almost zero. No other impurities were detected in the gases so the gas purity was better than 1 part in 1000.

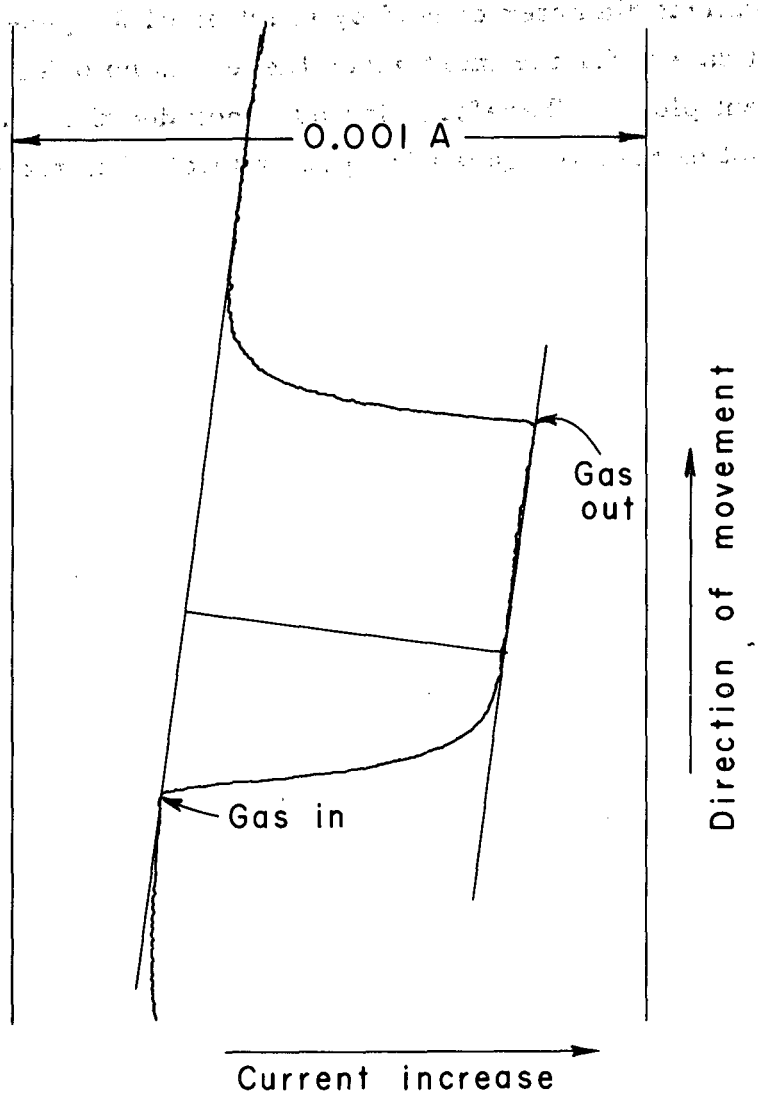

Fig. 3. Typical plot of filament current.

The shape of the energy-transfer curves is evidence of the gas purity. The filament current was very sensitive to small changes in filament diameter caused by reaction of the gases with the filament. In all cases, for the inert gases there was no offset in the filament-current plots. Therefore, it was concluded that there was a negligible amount of reactive gases (oxygen and water) in the gases used.

RESULTS AND DISCUSSION

The results of the energy-exchange experiments for neon, argon, nitrogen, carbon dioxide, and helium are shown graphically in Figs. 4, 5, 6, 7, 8, which are plots of energy loss per unit area of filament against gas pressure. The energy losses were calculated by use of Eq. (6).

The Alphatron vacuum gauge did not work well when helium was used. The gauge response was very slow and the pressure readings were erratic because the indicator fluctuated badly. Therefore, experiments were performed at only one temperature for helium. The results are shown in Fig. 8.

Energy exchange between oxygen and the tungsten filament could not be measured because the effect of the tungsten-oxygen reaction on the filament current masked any cooling effects. Figure 9 is a sketch of a typical recorder trace for oxygen; it is significantly different from Fig. 3, a typical trace for an inert gas. The current decrease shown in Fig. 9 was permanent. The decrease is attributed to reduction in the filament diameter by oxidation, with a consequent increase in the resistance.

Energy-exchange experiments using carbon dioxide were performed at 1860° and 2120° K. At 2120°K, reaction between carbon dioxide and tungsten became noticeable. A typical plot of filament current for the tungsten–carbon–dioxide system at 2120°K is shown in Fig. 10. The current decrease after the initial increase, due to the cooling of the filament by the gas, was caused by reaction of the carbon dioxide with the filament. A permanent current change after the gas is pumped out is also observed in this system.

The curves in Figs. 4 to 7 have a change in slope at about 1 μ pressure. The pressure at which the change in slope appears shows no regular variation with the filament temperature or with the different gases used. Also, the extrapolations of the power-loss curves do not

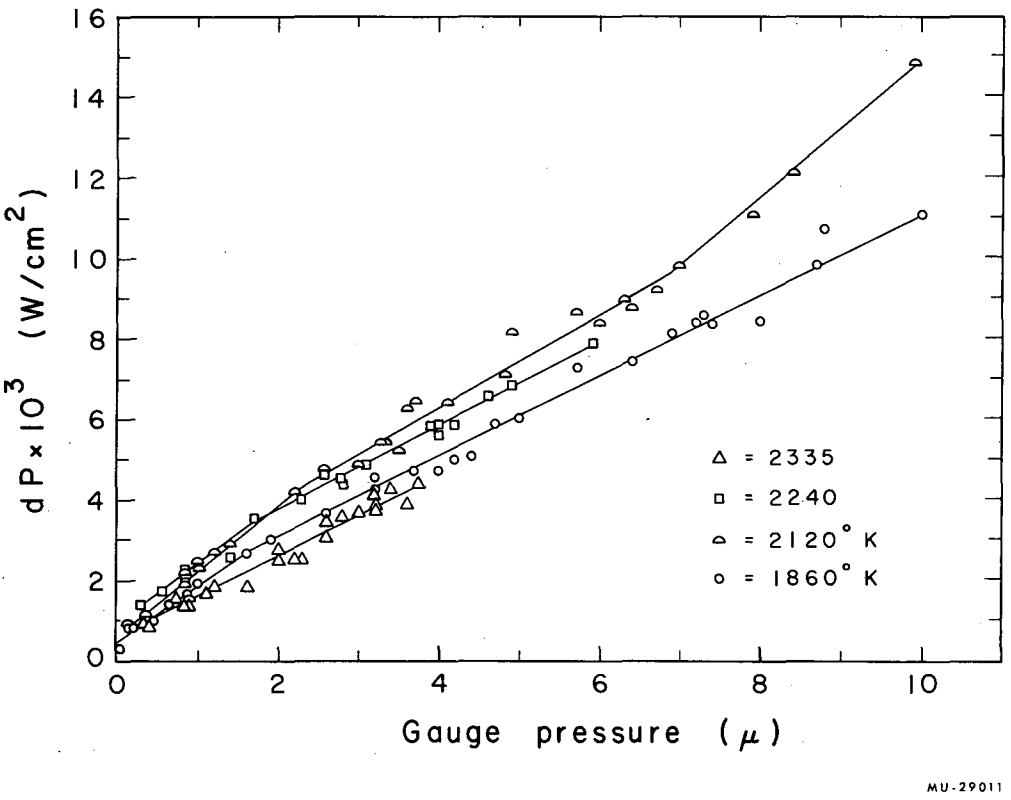

Fig. 4. Power loss vs argon pressure;
actual pressure = 0.840 × gauge pressure.

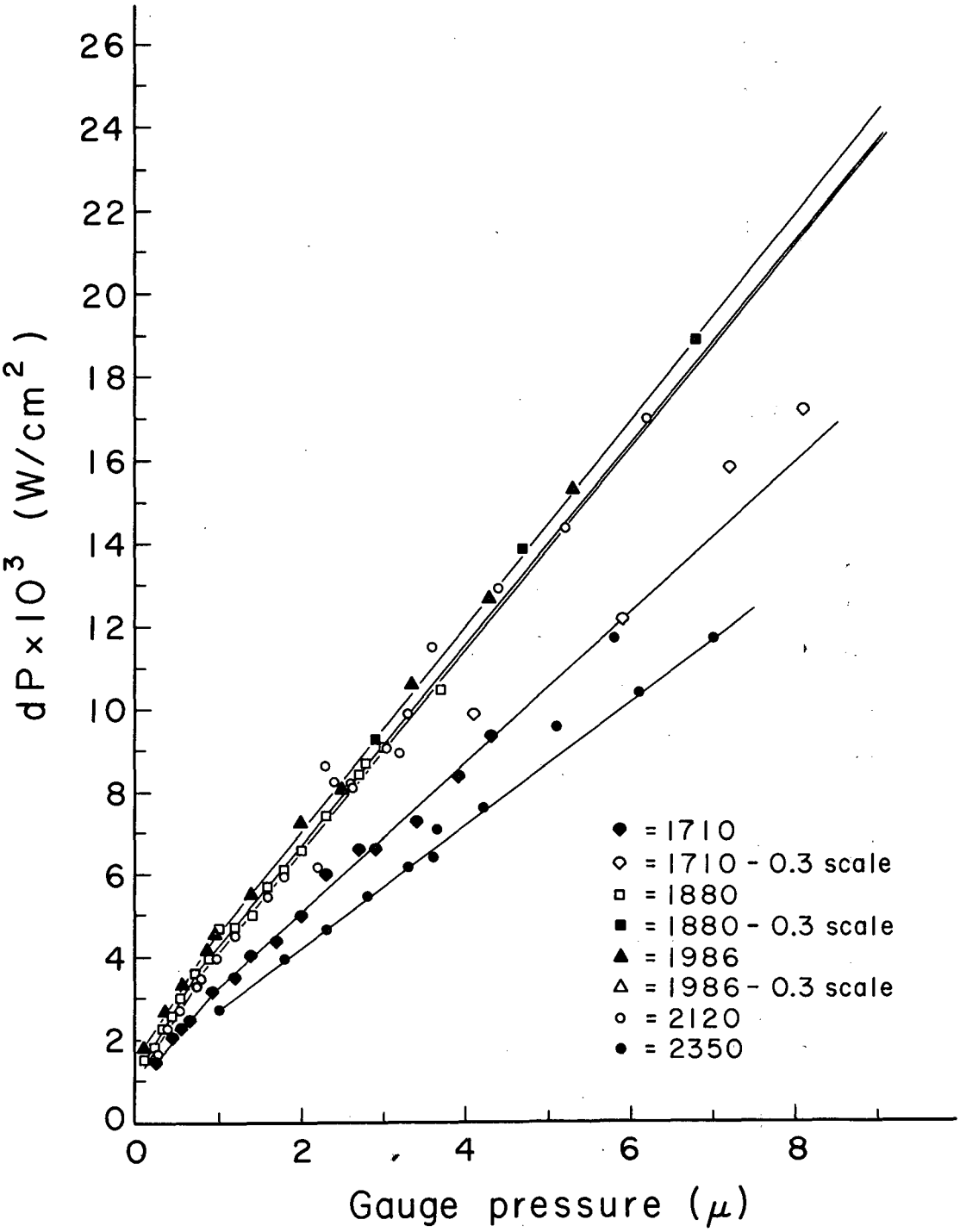

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Fig. 5. Power loss vs neon pressure;
actual pressure = 2.28 × gauge pressure.

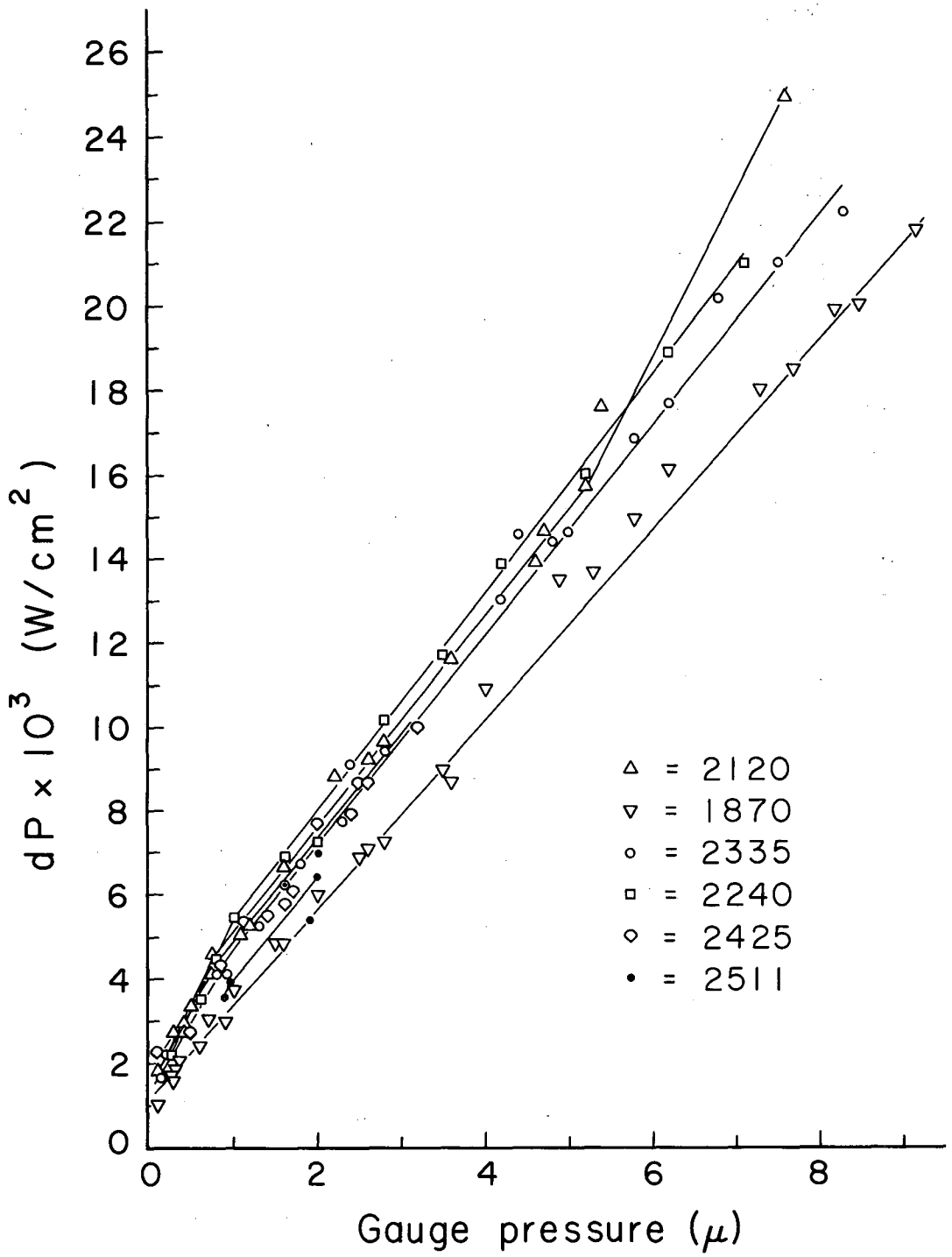

Fig. 6. Power loss vs nitrogen pressure; actual pressure = 1.04 × gauge pressure.

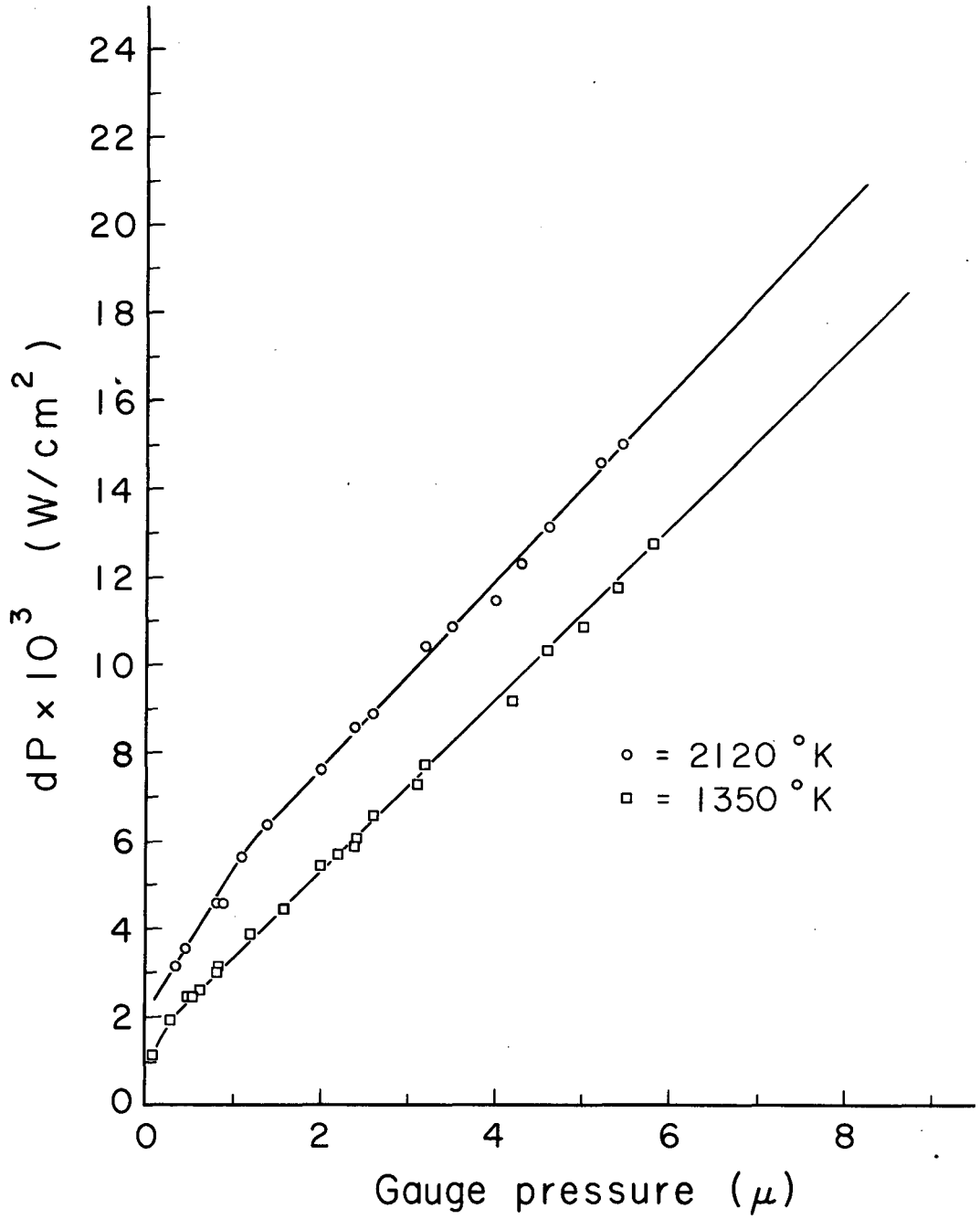

Fig. 7. Power loss vs carbon dioxide pressure; actual pressure = 0.633 × gauge pressure.

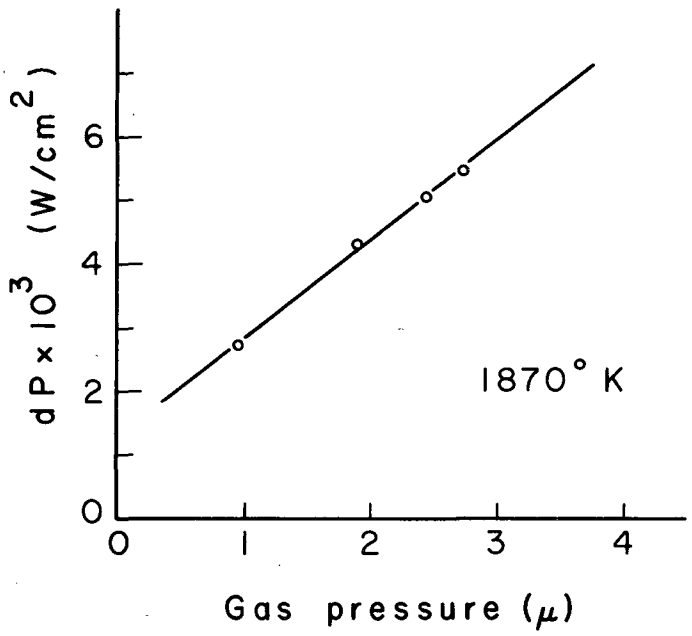

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Fig. 8. Power loss vs helium pressure.

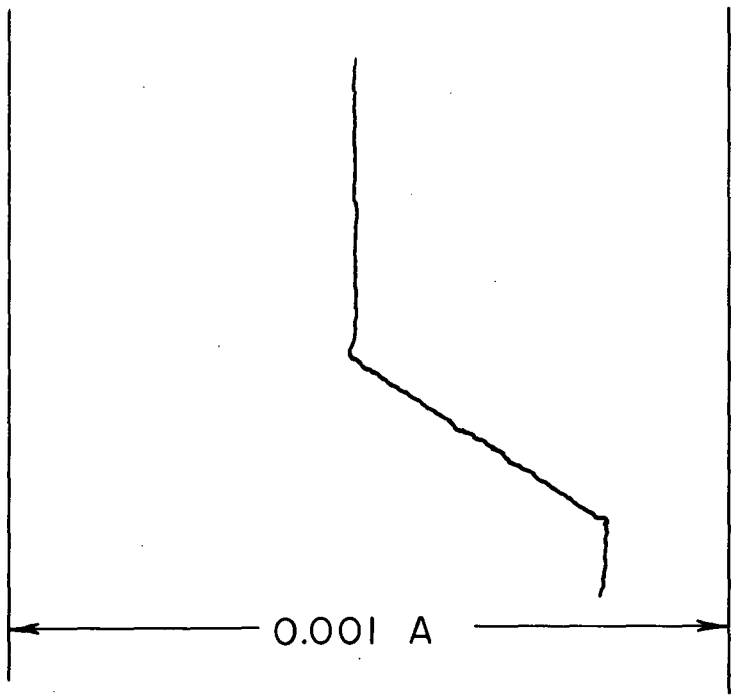

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Fig. 9. Sketch of recorder trace for oxygen.

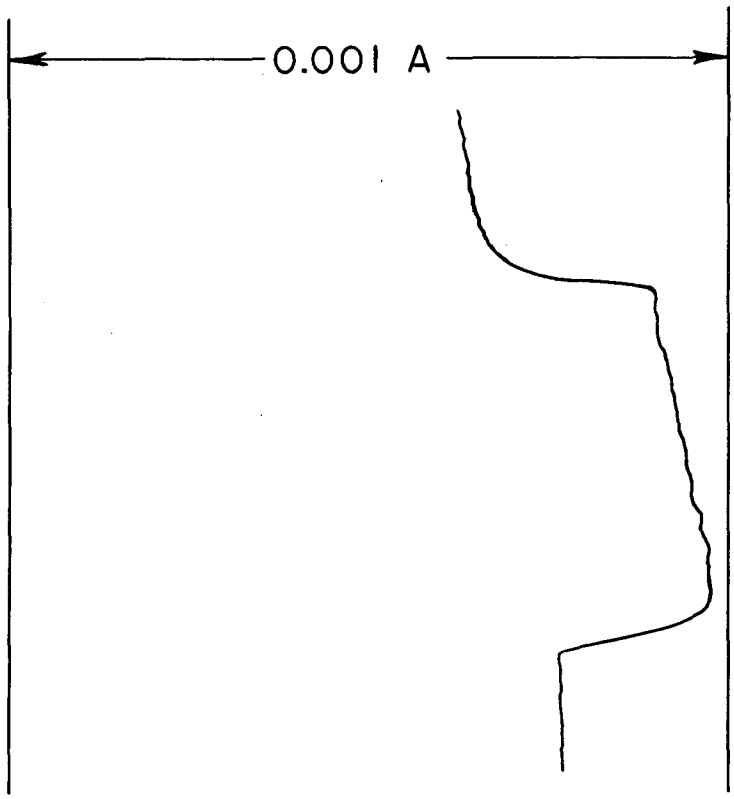

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Fig. 10. Sketch of recorder trace for carbon dioxide.

pass through the origin. Both these effects were probably caused by incorrect low-pressure readings resulting from the placement of the pressure gauge.

Figure 1 shows the position of the Alphatron gauge with respect to the reaction vessel. The gauge is at right angles to the tube leading from the reaction vessel, so that the gauge ionization chambers are a considerable distance from the reaction vessel. Furthermore, there is a cold baffle between the reaction vessel and the pressure gauges. Since the energy-exchange experiments were performed using a dynamic system this arrangement could cause the pressure readings to be lower than the actual pressure in the reaction vessel. The discrepancy would be less pronounced at higher pressures and could become essentially constant above 1 μ. A constant difference of from 0.5 to 2 μ between the reaction chamber pressure and the measured gauge pressure would explain the discrepancy.

From Figs. 4, 5, and 6 we see that:

(a) The power loss to the gas molecules is proportional to the gas pressure.

(b) The power loss does not seem to be simply dependent on the filament temperature or the difference between the filament temperature and the gas temperature.

(c) Within the possible experimental error, the slopes of the curves for power loss against gas pressure are nearly independent of temperature for each gas.

Since the power-loss curves do not go through the origin, the slopes of the plots of power loss versus gas pressure are used for W_c/p in Eq. (4) to calculate the thermal-accommodation coefficient. Values of these slopes and of the calculated thermal-accommodation coefficients α are given in Table II. Values of α are also plotted against temperature in Fig. 11. Because of malfunctioning of the electronic amplifier the thermal-accommodation coefficient obtained at 1710°K for neon is believed to be erroneous. It should be noted that the thermal-accommodation coefficients obtained for argon are very small compared with the value given by Thomas.

Table II. 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	0.087	0.095	437
Nitrogen	2120	2.50	0.083	0.082	451
Nitrogen	2240	2.60	0.081	0.077	457
Nitrogen	2335	2.50	0.0741	0.0733	451
Nitrogen	2425	2.49	0.0708	0.0701	450
Nitrogen	2511	2.45	0.067	0.0675	447
Average	-	2.466	-	-	449
Carbon dioxide	1860	1.975	0.136	-	512
Carbon dioxide	2120	2.15	0.126	-	528
Helium	1870	1.575	0.0359	-	356

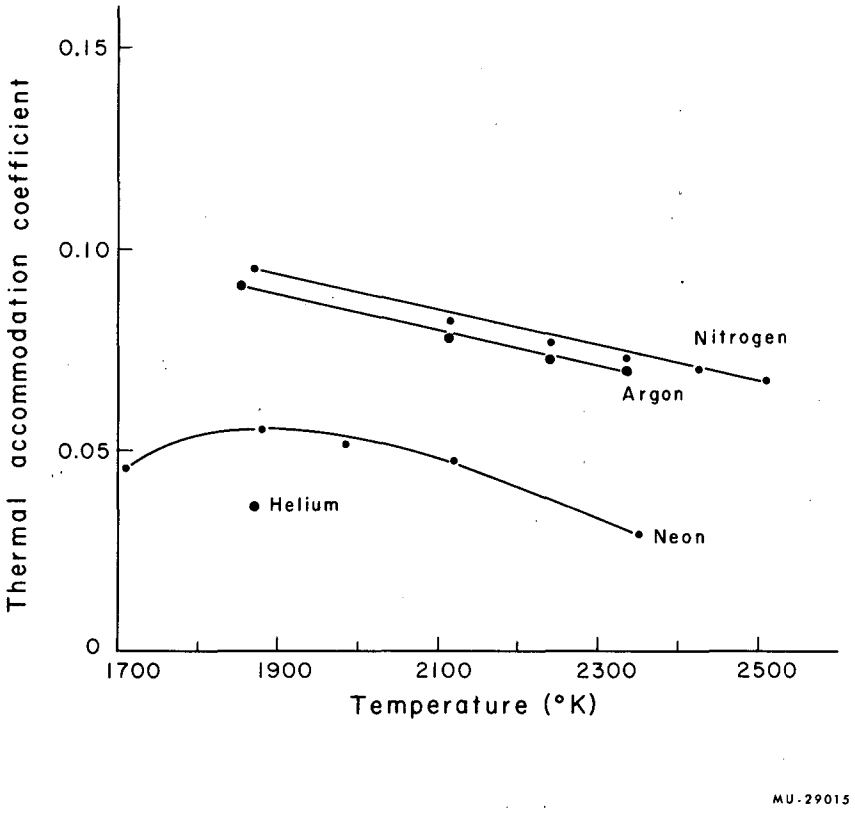

Fig. 11. Thermal accommodation coefficients vs temperature.

The thermal-accommodation coefficient is also defined as

$$(T_c - T_1)/(T_2 - T_1), \tag{7}$$

where T_1 is the temperature of the incident gas molecules, T_2 is the filament temperature and T_c is the temperature of the gas molecules when they leave the filament. From the values obtained for α, T_c can be calculated; T_c for the various gases is also given in Table II.

For helium on graphite, Meyer and Gomer found T_c to be 440°K, and for neon on graphite they found T_c to be 595°K. Since these temperatures are higher than the values found for helium and neon in this work, one can infer that all inert gases adsorb more strongly on graphite than on tungsten.

The relative magnitudes of these T_c values for different gases can be understood in terms of the relative van der Waals constants a for the different gases. Meyer and Gomer pointed out that to a first approximation the attraction between two different molecules due to van der Waals forces is given by the geometric mean of the van der Waals $\underline{a}$, where

$$a_{12} = (a_{11}\, a_{22})^{1/2} \tag{8}$$

For comparing the attraction between the tungsten surface and the different gases, a_{11} can be considered constant, whereas a_{22} depends on the gas. For a first approximation

$$\alpha \propto (a_{22})^{1/2}. \tag{9}$$

By comparing the square roots of the van der Waals $\underline{a}$ for the gases used, the relative magnitudes of the accommodation coefficients can be predicted. The magnitudes of the thermal-accommodation coefficients

are predicted by this approach to decrease in the order: (1) carbon dioxide, (2) nitrogen, (3) argon, (4) neon, and (5) helium. This is the order observed in Fig. 11.

With the background pressure of 4×10^{-6} mm that characterized the apparatus, the surface encountered by the gas molecules was covered by about one monolayer of chemisorbed oxygen atoms. The coverage is about one monolayer when the filament temperature is 2500°K, and remains the same as the temperature is lowered to 1710°K.

The forces between the surface and the impinging gas molecules are not strictly of the van der Waals type. True van der Waals forces result from induced dipole-induced dipole interactions. The atoms on the surface of the filament are polarized so that the forces between the filament and the gases result from the dipole-induced dipole interactions. Nevertheless, decrease in accommodation coefficient with increasing temperature supports the theory of Meyer and Gomer. The T_c calculated from the accommodation coefficients was constant from each gas, as shown in Table II.

The curves in Fig. 12 are comparisons of the power losses to the different gases from the filament at a constant temperature. At a constant temperature and for a given pressure, the energy exchange depends on the thermal-accommodation coefficient and on the number of gas molecules that strike the filament per unit area per time. The energy-exchange curve for helium lies above the curves for both neon and argon despite the low accommodation coefficient of helium, because of the high velocity of the helium atom.

The curves in Fig. 13 are plots of the power losses per collision with the filament for each kind of gas molecule. The heat capacities of the inert gases are all identical, so that the order of the curves in Fig. 13 gives an indication of the relative magnitudes of T_c for the inert gases.

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.

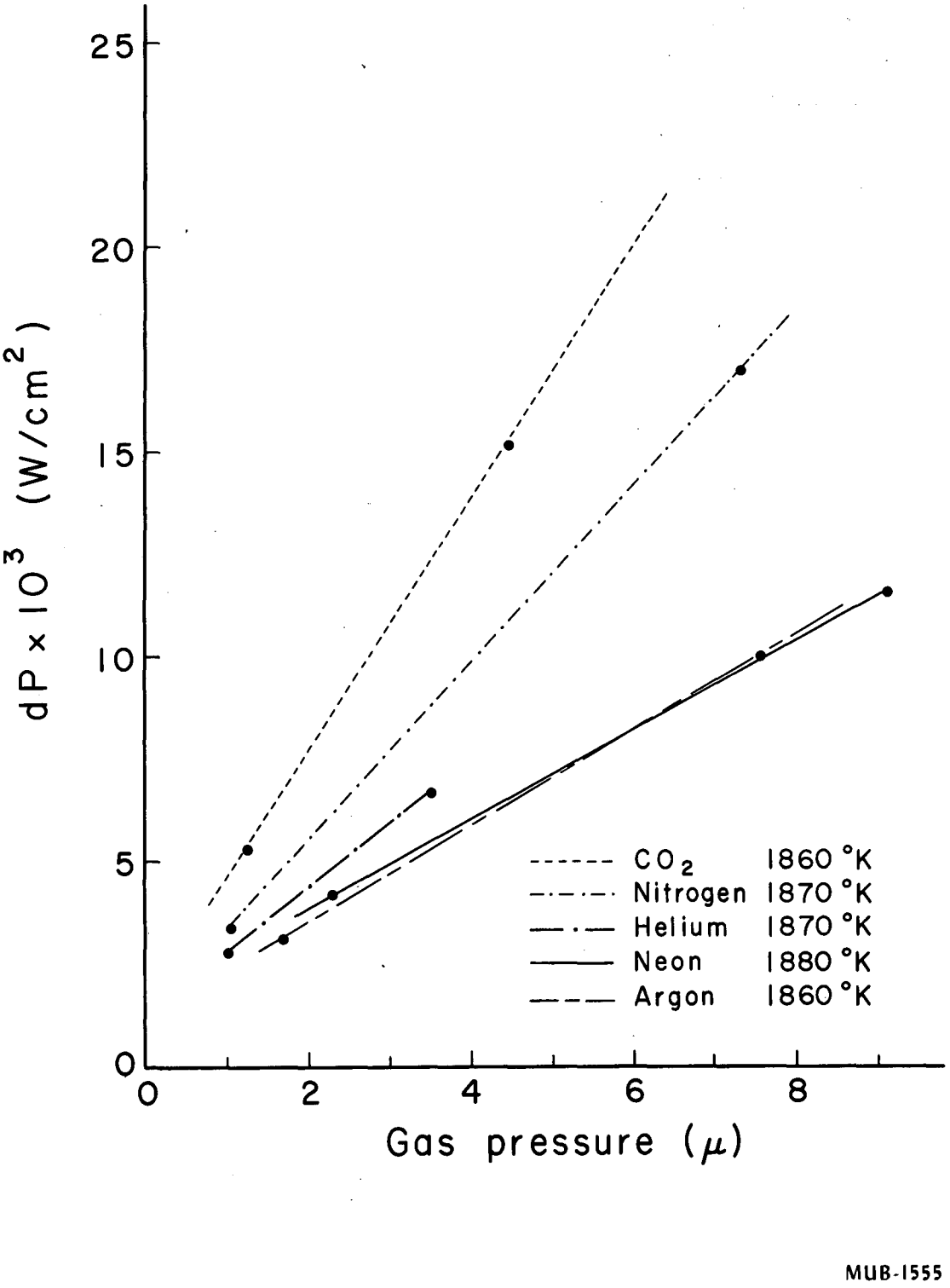

Fig. 12. Power loss vs gas pressure at 1870 ^{o}K.

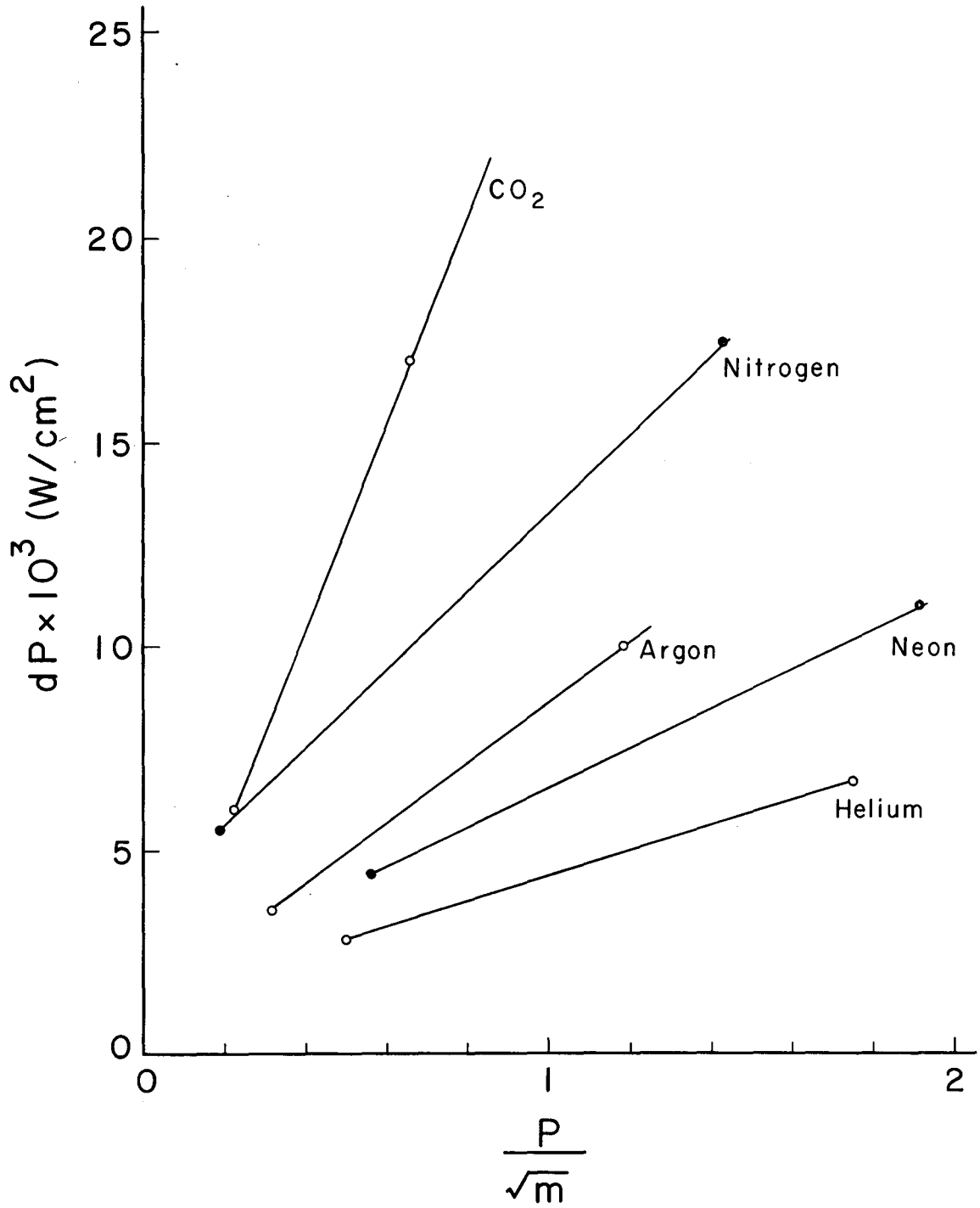

Fig. 13. Power loss per collision.

CONCLUSIONS

The exchange of energy between a cold gas and a hot tungsten surface is directly proportional to the gas pressure but is essentially independent of the filament temperature. The explanation given by Meyer and Gomer for their results on energy exchange between cold gases and a hot graphite surface also accounts for the results obtained in this investigation.[7] 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 certain "critical" temperature that is independent of the filament temperature. The critical temperatures for the gases used in this investigation lie between 350° and 550° K.

ACKNOWLEDGMENTS

The writer wishes to express his sincere thanks to Dr. Alan W. Searcy for his advice in carrying out this investigation; to Dr. David J. Meschi for his help with the equipment; to Dr. Harlan U. Anderson for his help and many suggestions on the experimental method used; to the University of California for a fellowship during the 1961-62 academic year, and to the Inorganic Materials Research Division.

This work was done under the auspices of the U. S. Atomic Energy Commission.

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