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The thermal accommodation coefficients of helium, neon, and argon on surfaces

Gerald Lee Zweerink

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THE THERMAL ACCOMMODATION COEFFICIENTS OF HELIUM, NEON, AND ARGON ON SURFACES

by

Gerald Lee Zweerink, 1943-

A DISSERTATION

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D. Vincent Roach
Advisor

B Ken Robertson

Raymond L. Venable

James L. [illegible], Jr.

OK Manuel

GF
update 8-16-90

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This dissertation has been prepared in the style utilized by *Surface Science*. Pages 3-14 contain the manuscript published in *Surface Science* *19*, 249-254 (1970). Pages 15-43 contain the manuscript to be submitted to *Surface Science* for publication. Appendices A, B, and C have been added for purposes normal to thesis writing.

ABSTRACT

Measurements of the accommodation coefficients of helium, neon, and argon on an ice surface at 77°K were accomplished, and the values are as follows:

T$^{\circ}$K	Accommodation Coefficients		
	He on Ice	Ne on Ice	Ar on Ice
77	0.47	0.73	1.00
216	0.25	0.39	0.45

Measurements of the accommodation coefficients of helium and neon on a clean tungsten surface are also reported here. These values were determined using the low pressure method and are given as follows:

T$^{\circ}$K	Accommodation Coefficients	
	He on Tungsten	Ne on Tungsten
300	.0181	
373	.0180	.054
403	.0217	.057
473	.0256	.060
523	.0271	.064
573	.0295	.076
623	.0315	.099

These data are compared with theoretical calculations of accommodation coefficients as well as with data from other experimental studies.

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INTRODUCTION

The research reported in this dissertation was accomplished in two phases. The first was a study of the accommodation coefficients of helium, neon, and argon on an ice surface at gas temperatures of 77°K and 216°K. The second part was a study of the accommodation coefficients of helium and neon on a clean tungsten surface as a function of gas temperature in the range of 300°K to 623°K.

The initial phase of the research was motivated by a need for knowledge of the efficiency of the energy transfer from the surface of a water droplet during its growth in a cloud chamber which contained an inert gas. An ice surface below 216°K was chosen so that existing low pressure methods for the determination of accommodation coefficients could be utilized. The experimental methods and results of this phase of the research are presented in Part I of the dissertation which is the manuscript as published in Surface Science 19, 249-254 (1970).

The second part of this research project was an attempt to develop a new method for the determination of accommodation coefficients of gases on a clean tungsten surface at high gas temperatures (that is, from room temperature to approximately 1000°K) and to carry out these determinations for helium and neon. The purpose of this project was to make available high temperature thermal accommodation coefficient data; thus providing an additional test for existing and future theoretical calculations which predict accommodation coefficients and their variations as a function of temperature. The experimental methods and results of this phase of the research are presented in Part II of the dissertation which is the manuscript which will be presented for publication in Surface Science.

The appendices contain material relevant to the research methods and results contained in the manuscripts of Parts I and II. Appendix A presents a historical background of thermal accommodation coefficients. Appendix B presents the development of the high temperature method of determining thermal accommodation coefficients. Appendix C is a justification for the linear plot used for the extrapolation of the apparent accommodation coefficient versus the inverse of ΔT.

PART I

THE THERMAL ACCOMMODATION COEFFICIENTS OF HELIUM, NEON, AND ARGON ON AN ICE SURFACE

Manuscript as published in Surface Science 19, 249-254 (1970).

Introduction

The interaction of gas atoms or molecules with surfaces is fundamental to the processes of nucleation, droplet growth and condensation. Experimentally these processes are often examined using cloud chamber techniques (1). Comparison of such experimental results with theory requires a knowledge of the efficiency of energy transfer among the various modes of motion of interacting species as well as vaporization and condensation coefficients. The relationships of the latter two coefficients with the thermal accommodation coefficient have been discussed by Winslow (2). The thermal accommodation coefficient (hereafter abbreviated A. C.) is defined as

$$\text{A.C.} = (E_r - E_i)/(E_s - E_i)$$

where E_i is the average energy flux (energy transferred across unit area in unit time) of a gas beam incident on a surface, E_r is the average energy flux of the beam after interaction and reflection by the surface, and E_s is calculated using kinetic theory and is the average energy flux of the reflected beam if the beam were to come into thermal equilibrium with the surface at temperature T_s before being re-emitted.

The work reported here was undertaken to determine the A. C. of several gases on water surfaces and may be of particular interest in light of investigations (3) of the process of water droplet growth as determined by expansion cloud chamber techniques. In such cloud chamber investigations water droplets are formed in an environment of an inert gas and, therefore, the A. C. of the inert gas at a water surface may play an important role in the process of nucleation and condensation. Specifically, the thermal A. C. of helium, neon, and argon on a solid water surface have been determined at two temperatures (77°K and 216°K) and are reported herein.

Experimental

The prinicpal apparatus consisted of a vacuum system with gas admitting equipment, an accurate McLeod gauge, an experimental tube (see Figure 1), an electrical system and a constant temperature bath.

The vacuum system was constructed entirely of Pyrex glass, except for the tube elements, and employed two mercury diffusion pumps in series, mercury cutoffs, and two cold traps between the last mercury cutoff and the experimental tube. The gas admitting system, separated by a mercury cutoff from the rest of the vacuum system had several mercury seal stopcocks lubricated with Apiezon N grease. The rare gases were of highest purity "Airco" grade.

The experimental tube is shown in Figure 1. A tungsten filament, 0.0037 cm in diameter and 20 cm long, is mounted along the axis of a cylindrical, 30 mm diameter, Pyrex tube. The tube is connected to the vacuum system through the upper side-arm and to a sealed capsule of water through the lower side-arm. The water sample was prepared in four steps. Deionized water was distilled from potassium permanganate and sealed in a vessel purged with water vapor. The distilled water, after two distillations under a vacuum of 10^{-6} torr, was sealed in the capsule which had a break-seal for subsequent introduction into the experimental tube.

Electrical measurements were made with a Leeds-Northrup K-3 potentiometer and suitable standard resistors. Current to the potentiometer and experimental tube was supplied by lead storage batteries.

The constant temperature bath consisted of a 25 liter Dewar flask filled with liquid nitrogen for the measurements at 77°K and filled with methanol for the measurements at 216°K. The cryogenic liquids were stirred with an immersed centrifugal pump type stirrer. For measurements at 216°K, the methanol was cooled through contact with a flask containing a slurry of dry ice and ethanol and the desired temperature maintained by use of two heating elements and a mercury-thalium contact temperature regulator.

The vacuum system was cleaned and treated, the filament annealed, and the filament characteristics determined in the manner described in Reference 4. The low pressure method (6) of determination of the A. C. was utilized in this work. The determination of the total power loss (W_T) per unit filament area with gas present, the power loss (W_V) per unit area under vacuum conditions, and the power loss ($W_G = W_T - W_V = E_r - E_i$) per unit area due to conduction by the gas from the surface has been described previously (4, 5). The A. C.

was calculated in the usual manner (4, 5) by dividing W_G by the power loss per unit area (E_s - E_i) which would be observed if the gas came to complete thermal accommodation with the surface. Two corrections to the A. C. determined in this manner were necessary. The presence of the gas alters the temperature gradient along the filament from the gradient existing during power loss in vacuum measurements and therefore the latter must be corrected to account for the alteration. This correction was made according to the procedure of Brown (7). A second correction to account for the pressure difference due to the thermal transpiration between the pressure gauge and the cryostat was made using the Liang formula (8).

After bakeout of the system and determination of the filament characteristics, but before breaking the water capsule to prepare the ice surface, the A. C. of helium on tungsten was determined at room temperature. If the magnitude of the A. C. of helium on tungsten and its rate of rise with time (5, 9) after flashing the filament were considered to indicate good vacuum conditions and a clean tungsten surface, the capsule was opened and the water surface prepared for measurements.

The solid water surface was prepared by distillation of water from the side-arm into the main chamber of the experimental tube with the latter at 77°K. Distillation was continued until the interior of the main chamber was covered. The entire experimental tube was then immersed in the constant temperature bath at 216°K. The water was vaporized from the filament surface by resistance heating. A new surface of solid water was formed by recondensation of water vapor after the filament was cooled. The walls of the experimental chamber were cooled to the desired temperature and measurements of the A. C. of the various gases on this surface were then completed. The cold trap adjacent to the experimental tube was kept at the temperature of the constant temperature bath (77°K or 216°K) for all measurements. The stopcock connecting the two cold traps was closed during each A. C. measurement at 216°K so that a constant water vapor pressure would be maintained. The pressure was measured before and after each measurement.

Discussion

The corrected experimental A. C. values are shown in Table 1.

Table 1

Accommodation Coefficients of Helium, Neon and Argon on Ice

Gas	Temperature = 216.5°K	Temperature = 77.35°K
He	0.25	0.47
Ne	0.39	0.73
Ar	0.45	1.00

Although the values are quite reproducible to one unit in the second decimal place, the authors wish to emphasize the possible errors inherent in these measurements. The experimental equipment and procedure is similar to that used previously (4, 5, 9) and therefore subject to the same possible sources of error. Two of these sources may be magnified in this work, particularly the determination of effective surface area. In previous work on metal surfaces, the assumption is made that the surface is smooth and that the apparent surface area, determined from length and average density, is the same as the effective surface area for impinging gas atoms or molecules. In the present investigation, the effective surface area of solid water was assumed to be the geometric area of the substrate. The second major difficulty in the present work is determination of the purity of the ice surface after the considerable manipulation necessary to produce a surface. However, existing contamination in the vacuum system was checked periodically. For example, in the 77°K measurements, the ice surface was desorbed by flashing and the A. C. of helium determined as a check against the accepted clean surface values (9).

The temperature dependence of the A. C. of helium on the ice surface is of particular interest. In the temperature range 77-216°K, the A. C. of helium, to the authors' knowledge, has been observed to increase with increasing temperature in all systems examined (10). For helium on clean tungsten an increase with decreasing temperature has been recorded for temperatures below 40°K. The behavior reported here for helium on ice is qualitatively similar to that predicted by the Devonshire theory (11) of accommodation in calculations by Gilbey (12) for a gas (mass 4 a. m. u.) impinging on a solid (mass 100 a. m. u. and Debye temperature of $50^{o}K$) and interacting through a Morse potential with k = $2\mathring{A}^{-1}$ and D = 0 - 100 cal mole^{-1}. Calculations using Devonshire theory have been made for the system of helium (mass = 4 a. m. u.) on solid water (mass = 18 a. m. u. and Debye temperature of $140^{o}K$) interacting through a Morse potential with k = $1.3\mathring{A}^{-1}$ and for various values of D. In view of the approximation in the transition probability in the Devonshire theory (13) which results in an error in the resulting A. C. formula (14), the calculated values of the A. C. are too large by a factor of two to three and therefore the calculated magnitude is not so much of interest as the behavior of the A. C. with temperature. These calculations indicate that a value of D = 325 cal mole^{-1} yields reasonable variation of the A. C. of helium with temperature. However, the calculations which produce this variation must be made with the reservations that (1) the error in the calculated transition probability and therefore in the calculated A. C. is temperature dependent and (2) that a change in roughness of the ice surface, e.g. with a change in surface temperature, can effect a change in the A. C. of helium.

No attempt was made to compare other theories of thermal accommodation with experimental values reported herein, as this is primarily a report of experimental results. Of particular interest would be calculations using the classical theories (e.g. Goodman (15), Trilling (16), etc.) and the Goodman-Wachman (17) interpolation formula.

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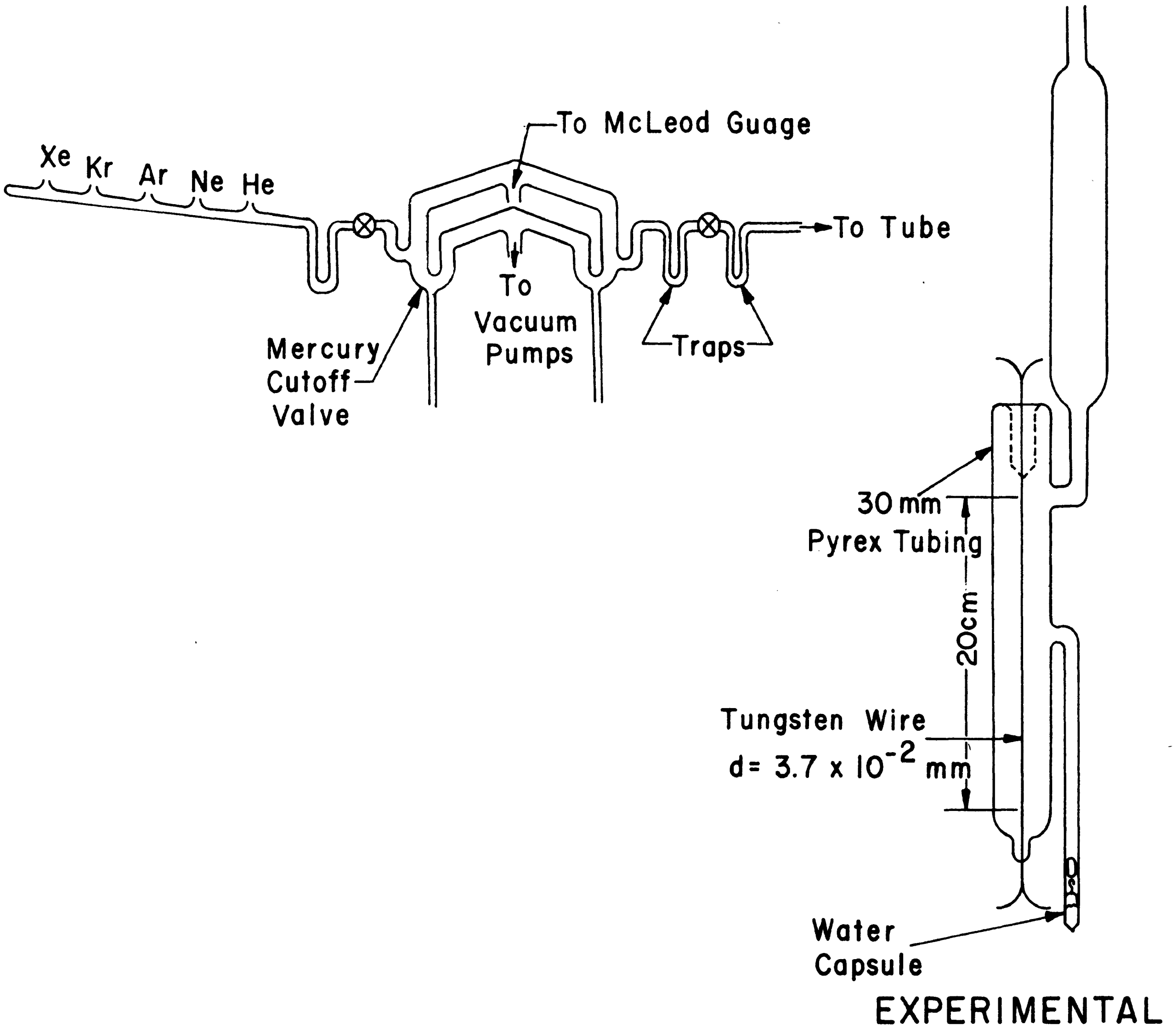
FIGURE 1

EXPERIMENTAL TUBE AND VACUUM SYSTEM



EXPERIMENTAL
TUBE

FIGURE 1

PART II

THE THERMAL ACCOMMODATION COEFFICIENTS OF HELIUM AND NEON ON A TUNGSTEN SURFACE FROM 300°K TO 623°K

Manuscript to be submitted to *Surface Science*.

Introduction

The thermal accommodation coefficient (hereafter abbreviated as A. C.) as defined in terms of the average energy flux (energy crossing a unit area per unit time) is expressed by the equation

$$\text{A.C.} = (E_r - E_i)/(E_s - E_i).$$

E_i is the average energy flux of an incident stream of atoms to the surface, E_r is the average energy flux of the stream of atoms leaving the surface, and E_s is the average energy flux of a stream of atoms leaving the surface corresponding to the temperature of the surface.

Roberts (1), in his study of the A. C. of helium on a tungsten surface, noted that the value of the A. C. depended greatly on surface conditions. By the use of high vacuum techniques to control the surface contamination rate, he was able to reduce the value of the A. C. of helium on tungsten from .19 to .05. Later Thomas (2) and coworkers (3,4) reported clean surface A. C. values of the noble gases on tungsten as a function of temperature from 77°K to 303°K. These A. C. determinations were accomplished under gettered conditions and the values for helium were significantly lower than those reported by Roberts. The value reported by Thomas for helium on tungsten at 303°K was .0167. The determinations of the A. C. on tungsten were extended to 473°K by Wachman (5) in 1966. More recently, Krueger

(6) has studied the A. C. ratio of helium <u>4</u> to helium <u>3</u> as a function of temperature from 77°K to 513°K.

To date, all A. C. determinations were made in glass walled conductivity cells, thereby having an upper limit of about 513°K for clean surface determinations. This limit is caused primarily by the outgassing of water from the glass. Thomas and Roach (7) used the temperature jump pressure region for the determination of the A. C. of helium, neon, and argon above 300°K to avoid the problem of contamination from the glass walls of the conductivity cell. The results, however, were ambiguous because of the different methods of calculation of the A. C. in the temperature jump region.

In order to overcome these problems, a new method for determining the A. C. to 623°K in the low pressure region was developed, and the results are presented in this paper.

Apparatus and Experimental Procedure

The apparatus consisted of an ultrahigh vacuum system with a gas admitting side arm, an accurate McLeod gauge, an electrical system, a thermal conductivity cell newly designed for high gas temperatures (300°K to 623°K), and a constant temperature bath to cool the vacuum envelope of the thermal conductivity cell.

The vacuum system (Figure 1) was constructed of pyrex tubing with two single stage mercury diffusion pumps in series. Two mercury cutoff valves were used to contain the desired gases in the system; one being used to isolate the stopcocks of the gas admitting system from the measurement system. A trap containing activated charcoal and cooled with liquid nitrogen was used to clean the helium or neon to eliminate active gases before admission of the gas into the measurement system. The conductivity cell was separated from the mercury cutoff valves and the diffusion pumps with a double U-tube liquid nitrogen trap. The gas in the measurement system was cleaned with a mischmetal getter located between the cold trap and the conductivity cell. A getter tube was attached directly to the conductivity cell with 20 mm pyrex tubing.

The constant temperature bath, a pyrex cylindrical container 28 cm in diameter and 60 cm tall filled with transformer oil, was maintained at 26°C. It was cooled by chilled water flowing at a constant rate through copper tubing coils in the bath and heated with a coiled immersion heater controlled by a Fisher proportional temperature control (capable of temperature control to 0.01°C).

The cell (Figure 2) was a cylinder 23 cm long and 20 mm in diameter, constructed of .001 inch molybdenum sheet with a filament of tungsten wire .0037 in diameter and 16.5 cm long mounted coaxially in the cylinder to temperature regulated leads. These leads to the filament inside the conductivity cell were constructed from .05 inch tungsten rod about 3 cm in length, over which were placed quartz sleeves for electrical insulation (8). Tungsten wire .006 inch in diameter was wound over the sleeves as the heaters for the leads. Thermocouples of tungsten, 3%-rhenium; tungsten, 25%-rhenium were used to monitor the temperature of the leads. The top lead was connected to the cylinder with a tungsten rod through a quartz loop on the end. The quartz loop provided electrical insulation between the cylinder and the lead. A small molybdenum leaf spring was used to connect the bottom lead to the cylinder and keep the filament inside the cell straight. Current was passed through the temperature controlled leads to the filament and like arms of the thermocouples were used as potential leads. The current to the filament was supplied by a lead storage battery and electrical measurements were made with a Leeds-Northrup K-5 potentiometer and a 10 ohm standard resistor.

Two thermocouples of tungsten, 3%-rhenium; tungsten, 25%-rhenium were attached to the inside of the molybdenum cylinder through a tantalum spot weld (9). They were placed on opposite sides of the cylinder, one 7.5 cm from the top and the other 7.5 cm from the bottom. These thermocouples were used to monitor the temperature of the cylinder walls.

Two radiation shields were attached to the cylinder to protect the filament inside from direct radiation. The shields were molybdenum cylinders 25 mm in diameter, one 7.5 cm in length for the top of the cylinder, the other 1.8 cm in length for the bottom.

The cell was then mounted coaxially in a cylindrical pyrex glass vacuum envelope 57 mm in diameter, which contained three hairpin heating filaments arranged symmetrically around the conductivity cell. The cylinder position was adjusted so that the temperature distribution along the heating filaments adjacent to the cylinder was as even as possible. At 2600°C the heating filament would radiate 1000 watts of power.

A 0-20 amp, 0-60 volt Kepco current regulated power supply was used to power the heating filaments. Two 0-25 volt and 0-1 amp voltage regulated power supplies in series with 15 ohm power resistors were used to power the lead heaters. Temperature regulation was ± .02°C for the leads and cylinder walls. The temperature control was accomplished by monitoring the thermocouples with a Leeds-Northrup K-3 potentiometer and adjusting the power supplies manually.

The molybdenum cylinder, along with the attached heat shields and thermocouples, was heated to 2000°C in a vacuum chamber by means of an induction heater to outgas H_2 from the metal parts. The conductivity cell was then assembled and attached to the vacuum system. Once assembled, the system was cleaned by baking the conductivity cell and traps at 400°C for eight hours and flaming the rest of the system with a gas-air torch for fifteen minutes of every hour during the bakeout (10). This was followed by the heating and cleaning of the molybdenum cylinder and its components at a temperature of 1100°C by electron bombardment from the heating filaments with an accelerating voltage of + 600 v and an electron current of 450 ma. Cleanup of the molybdenum cylinder was carried out for two hours with the liquid nitrogen over the U-tube on the mercury side of the double U-tube trap.

These two procedures were followed alternately through three bakeouts and two cleanups by electron bombardment (11). The cylinder was then cleaned by electron bombardment for fifteen minutes, followed by deposition of a small amount of mischmetal. The mischmetal mirror was baked and flamed into the nearest U-tube of the trap. Both U-tubes of the trap were then immersed in liquid nitrogen and a diffuse layer of mischmetal was deposited on the walls of the getter cell (12). The tungsten filament was then annealed at 2700°C for two hours to insure stable resistances on flashing to 2400°C and also to remove extrusion marks from the filament (Figure 3) for more accurate surface area calculations.

The A. C. determinations of helium on the tungsten filament surface at 26°C were made after flashing the filament to check the contamination of the system. If the change in the A. C. with time or in magnitude was too great, the cylinder was cleaned for ten minute periods by electron bombardment until the change with respect to time and magnitude, was within acceptable limits as reported in reference 2. Accommodation coefficients were then determined at higher temperatures using procedures similar to those described by Wachman (6) with corrections that will be discussed later.

During the development of the thermal conductivity cell used for these measurements it was found that the temperature of the central filament was raised, by direct radiation from the heating filaments, to a higher temperature than the molybdenum walls of the cell. By adding the radiation shields at the top and bottom of the cylinder, the temperature difference was decreased by a factor of three. This discrepancy between the filament and wall temperatures was still too great for accurate A. C. determinations. Therefore, corrections were made for the difference between the temperature of the filament when no current was passing through it while the cell was evacuated, and the temperature when the gas was present. This was done by adjusting the calibration curves of power versus resistance to intercept the same resistance at zero power input. This enabled an initial approximate calculation of the A. C., but still a small amount of power loss due to the gas and part of the temperature difference was undetermined.

The apparent A. C. was calculated in the usual manner (10). First, the power loss per unit area (W_v) under vacuum conditions was determined from the adjusted filament resistance versus power loss in vacuum curve. The total power loss per unit area (W_t) was determined with gas present, yielding the power loss per unit area due to the gas ($W_g = W_t - W_v = E_r - E_i$) (5). Dividing W_g by ($E_s - E_i$), the amount of power transferred per unit area, if complete thermal accommodation occurs, yields the apparent A. C. A linear plot of the apparent A. C. at constant gas pressure versus the inverse of the apparent temperature difference (ΔT) from the A. C. calculation was made and the intercept, as the inverse of ΔT went to zero, was taken as the correct A. C.

There were two additional corrections for the A. C. determined in this manner. The first, to account for the pressure difference between the gauge and the heated cell due to thermal transpiration, was made according to the equation of Takaishi and Sensui (13). The second to account for the change in the thermal gradient over the filament from evacuated conditions to conditions when gas was present was made according to the calculations of Brown (14).

The thermal transpiration corrections for helium ranged from 4% at 373°K to 14% at 623°K with the McLeod gauge at 25°C. For neon, the transpiration corrections ranged from 3% at 373°K to 11% at 623°K. The end loss corrections for both helium and neon ranged from 13% at 373°K to 9% at 623°K.

Another possible source of error in these calculations, giving rise to a third correction, is a mercury pumping effect. This effect is caused by mercury streaming from the McLeod gauge to the cold trap, thereby increasing the gas pressure in the conductivity cell. The data presented here were not corrected for the mercury streaming effect, as most other reliable data are not. According to Viney (15), a correction of 2.6% could be applied to increase all of the helium pressures. Further, a 4.25% correction to increase the neon pressures could be applied. These corrections are for a McLeod gauge at 25°C with a tube 10 mm in diameter connecting the gauge to the trap.

Discussion

The A.C. measurements reported in this paper are the first results available from room temperature to 623°K using the low pressure method of determination. Previous measurements have only been reported to 513°K due to contamination problems above this temperature. These results will be compared with those of other researchers and with theoretical calculations. In Table 1, the values for the A.C. of helium and neon on tungsten are given along with the pressures at which these values were determined. The errors inherent in these determinations are the same as in those of the data with which they are compared. The size of the errors may be slightly larger due to methods used to correct for temperature errors caused by radiation. Figure 4 is a plot of the helium A.C. values compared with those determined by Wachman, Thomas, Silvernail, and Krueger using the low pressure method. Values determined by Thomas and Roach, using the temperature jump method are also compared here.

At 300°K the results of these determinations correspond closely to data reported by Thomas, but diverge at higher temperatures from values given by Krueger. The data reported by Thomas and Roach using the temperature jump method and calculated according to Kennard compare well with the data presented here. However, the same data reported by Thomas and Roach using the Harris method of calculation agrees more nearly with that reported by Krueger. The values presented here are slightly higher than the other results with which they are compared, possibly due to the fact that an ungettered conductivity cell was used.

Figure 5 shows a plot of the neon results as compared with the data of Thomas, using low pressure methods, and of Thomas and Roach, using the temperature jump method calculated according to Kennard. These data compare quite well up to a temperature of approximately 513°K at which point a large increase in the neon A. C. is observed from this work. This increase has not previously been predicted by theoretical calculations or observed experimentally. Previous to and following each neon A. C. determination a helium A. C. determination was made. The fact that the helium measurements yielded clean surface A. C. values indicates that the increase noted in the neon A. C. as a function of temperature is a real effect.

A comparison of the helium A. C. results presented in this paper, with classical theoretical calculations given by Goodman and Wachman (16), and Trilling (17), and with a quantum mechanical theory by Devonshire (18), is given in Figure 6. The parameters suggested by the author of each theory are the ones used in the calculations, with the exception of the Devonshire calculations. In this case, scaling factors (.333 and .467) and the parameters suggested by Roach and Harris (19) for helium are used. As D (the well depth for the Morse potential) in the Devonshire formula decreases, the theory corresponds more closely to the data as is shown in Figure 7. Goodman and Wachman's theoretical calculations correspond most nearly to the data reported here, though none of the calculations increase with temperature as greatly as these data.

In Figure 8 the neon data are compared with the same theories as were the helium results. In this case, the parameters are those suggested by the author of each theory, excepting the Devonshire calculations where the parameters used are consistent with those of the other two theories. For the Devonshire calculations a scaling factor (.356), as suggested by Roach and Harris, is again chosen to correct the calculated values. The agreement of the theories up to 500°K with the data is quite close, while Trilling's calculations follow the trend of the presented data best of the three. Neither the Goodman-Wachman or Devonshire theories predict as rapid an increase of the A. C. with temperatures beyond 500°K as observed here.

The A. C. as temperature increases should approach the hard sphere collision A. C. limit as given by Baule (20).

$$\text{A. C.} = (2mM)/(m + M)^2$$

where m is the mass of the gas atom and M is the mass of the surface atom. This would be .043 for helium and .178 for neon. These data appear to be increasing to these values more rapidly than predicted by the three theories reviewed here, particularly the neon data.

Summary

This paper has presented new data for the A. C. of helium and neon on tungsten. The data are to higher temperatures than attempted previously using the low pressure method and should provide a good test for theoretical calculations.

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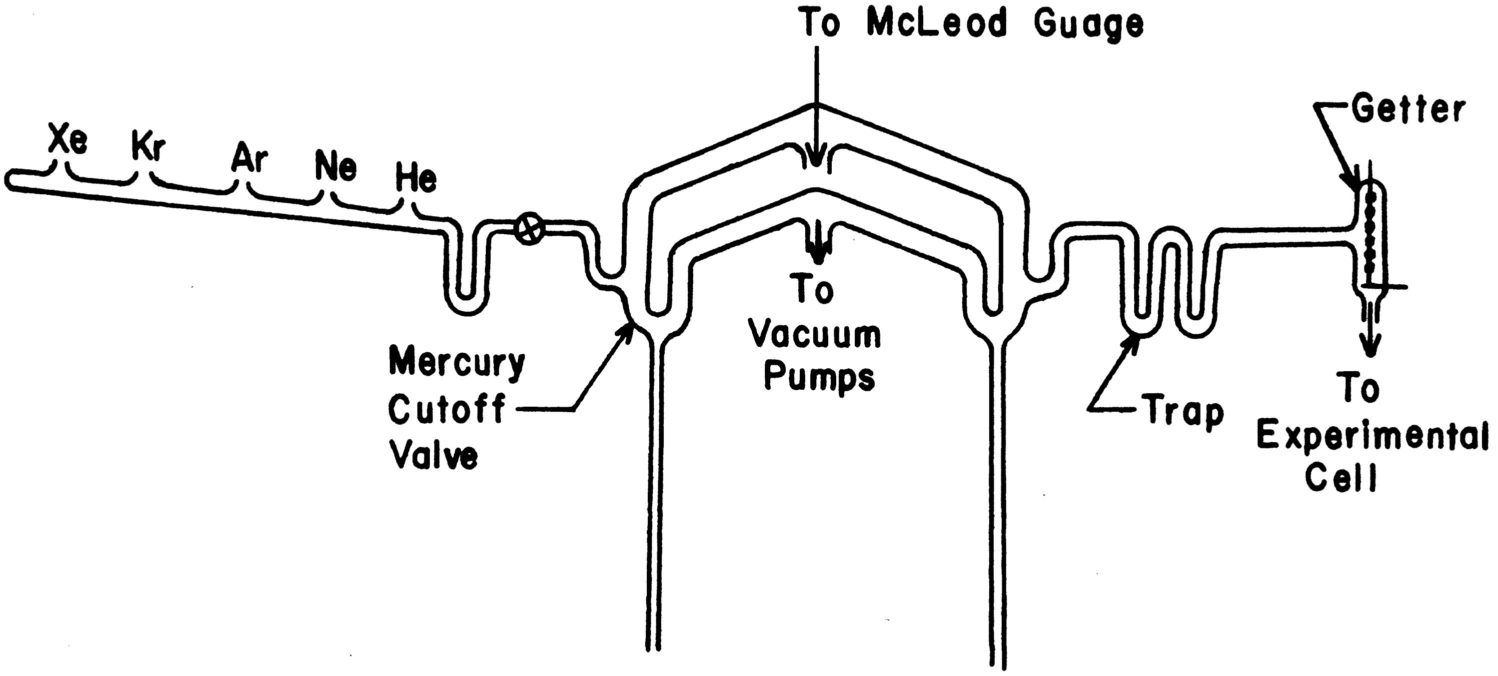
Table 1

Values of the Accommodation Coefficient of Helium and Neon on Tungsten

T°K	P. in mm	A. C. He	P. in mm	A. C. Ne
300	.0299	.0181		
373	.0326	.0180	.0338	.0540
403	.0328	.0217	.0342	.0556
473	.0302	.0256	.0300	.0598
523	.0350	.0271	.0346	.0641
573	.0317	.0295	.0282	.0760
623	.0305	.0315	.0321	.0991

FIGURE 1

VACUUM SYSTEM



VACUUM SYSTEM

FIGURE 1

FIGURE 2

EXPERIMENTAL CELL

A. Molybdenum cylinder supports

B. Upper radiation shield

C. Upper lead heater with quartz insulator

D. W-25% Re; W-3% Re upper lead thermocouple

E. W-25% Re; W-3% Re cylinder thermocouple

F. Measurement filament

G. Molybdenum cylinder

H. Heating filament

I. W-25% Re; W-3% Re cylinder thermocouple

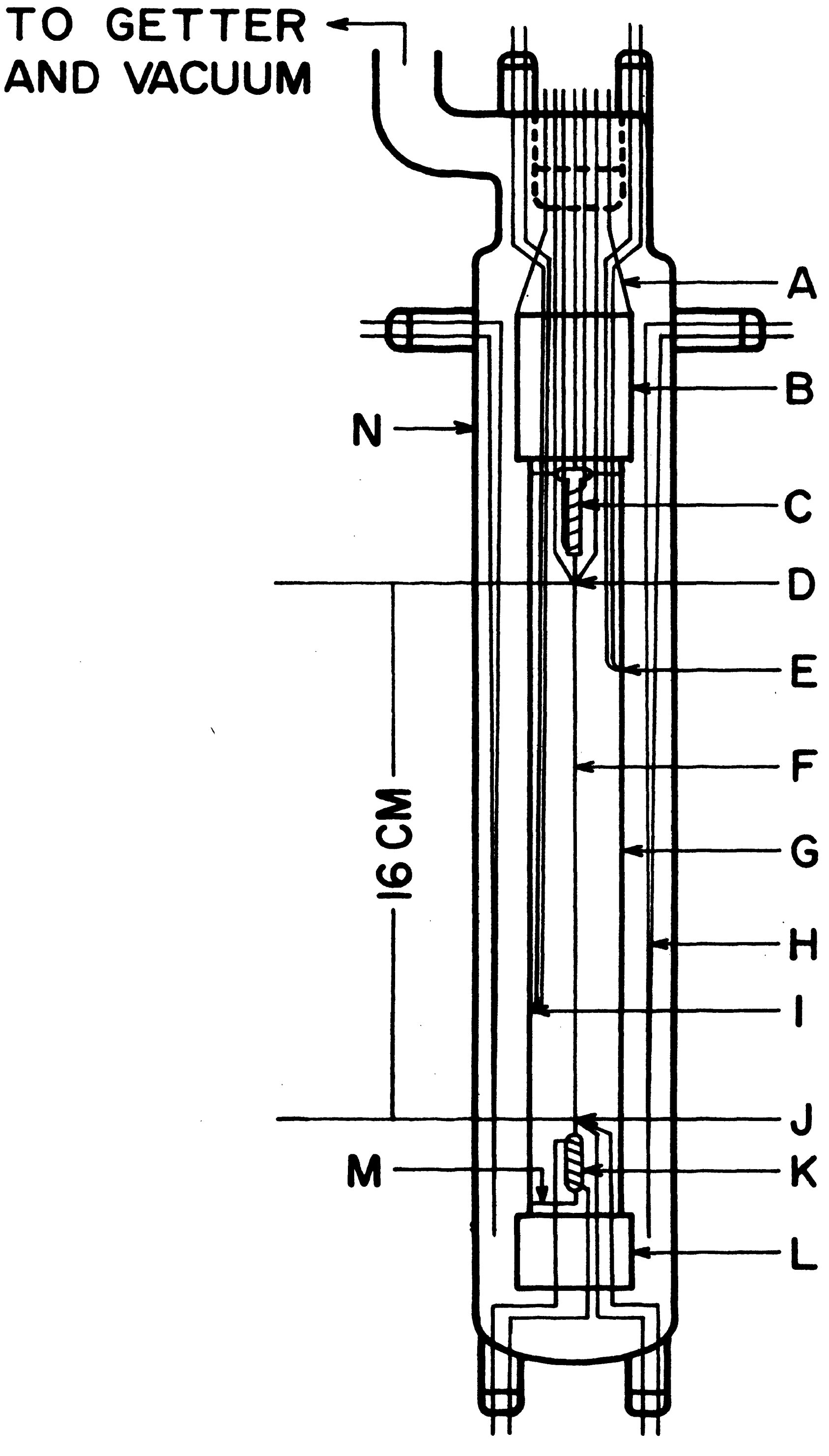
J. W-25% Re; W-3% Re lower lead thermocouple

K. Lower lead heater

L. Lower radiation shield

M. Leaf Spring

N. 57 mm pyrex glass vacuum envelope



EXPERIMENTAL CELL

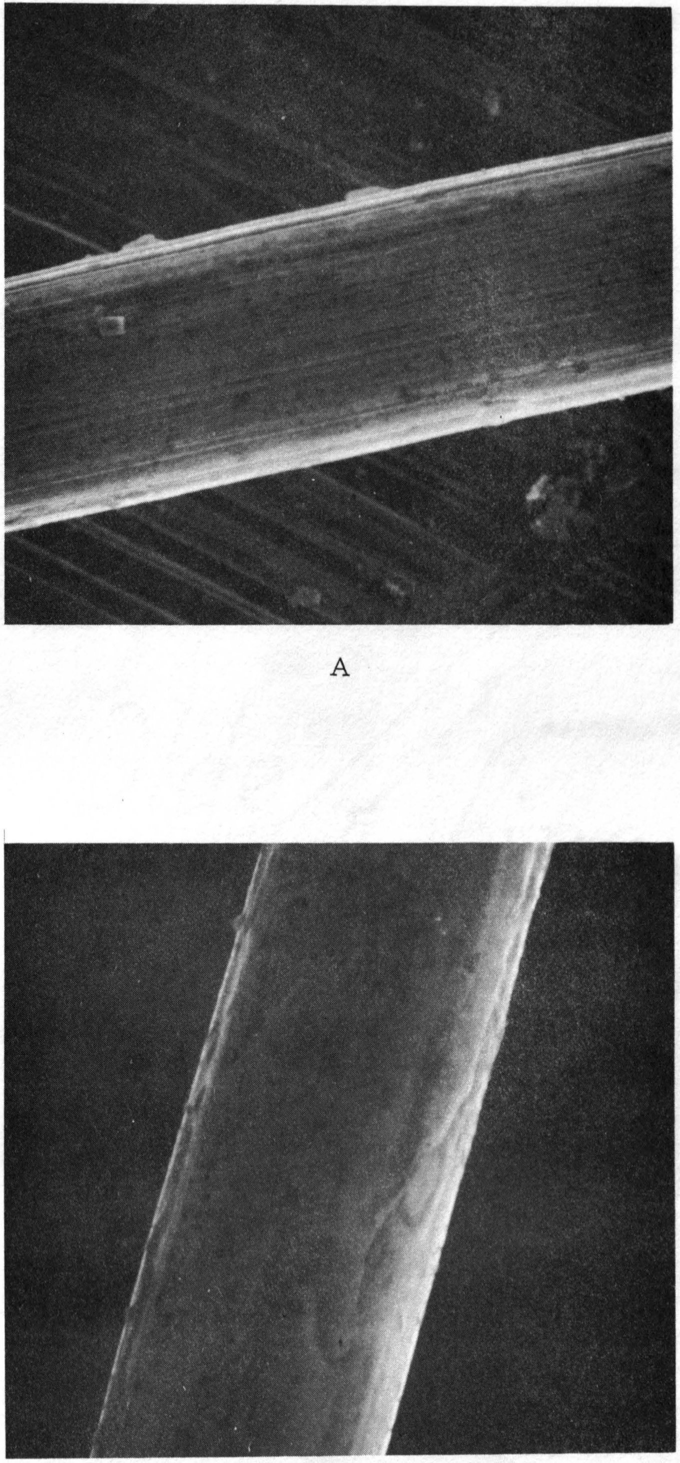
FIGURE 2

FIGURE 3

MEASUREMENT FILAMENT SURFACE

A. Unannealed tungsten filament 3.7 x 10^{-2} mm in diameter magnified 1000X

B. Annealed tungsten filament 3.7 x 10^{-2} mm in diameter magnified 1000X



A

B

FIGURE 3

FIGURE 4

EXPERIMENTAL RESULTS FOR HELIUM COMPARED WITH EXISTING EXPERIMENTAL RESULTS

□ This work

○ Thomas

△ Wachman

◇ Thomas and Krueger

▽ Thomas and Roach (Kennard, temperature jump method)

♀ Thomas and Roach (Harris, temperature jump method)

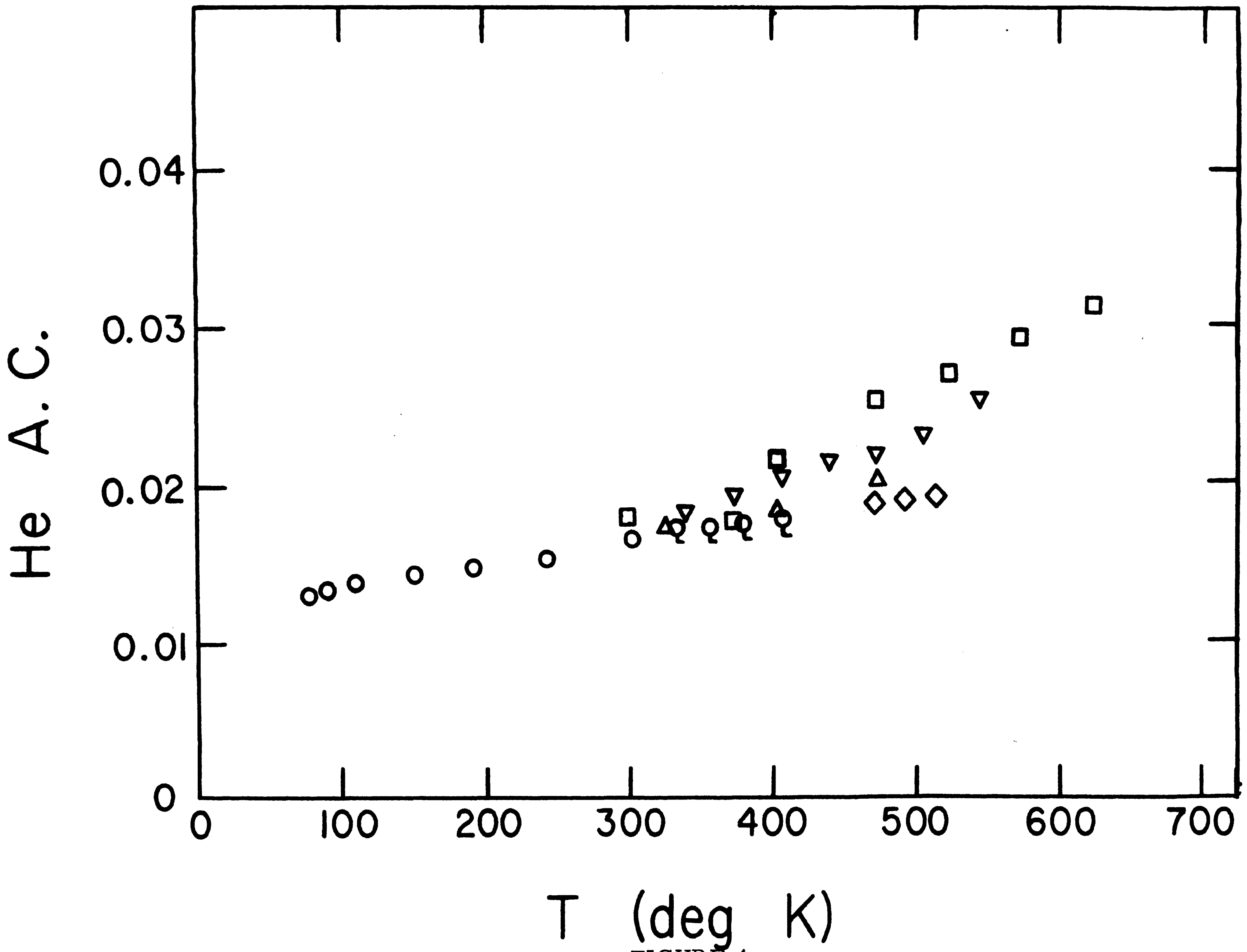


FIGURE 4

FIGURE 5

EXPERIMENTAL RESULTS FOR NEON COMPARED WITH EXISTING EXPERIMENTAL RESULTS

□ This work

○ Thomas

▽ Thomas and Roach (Kennard, temperature jump method)

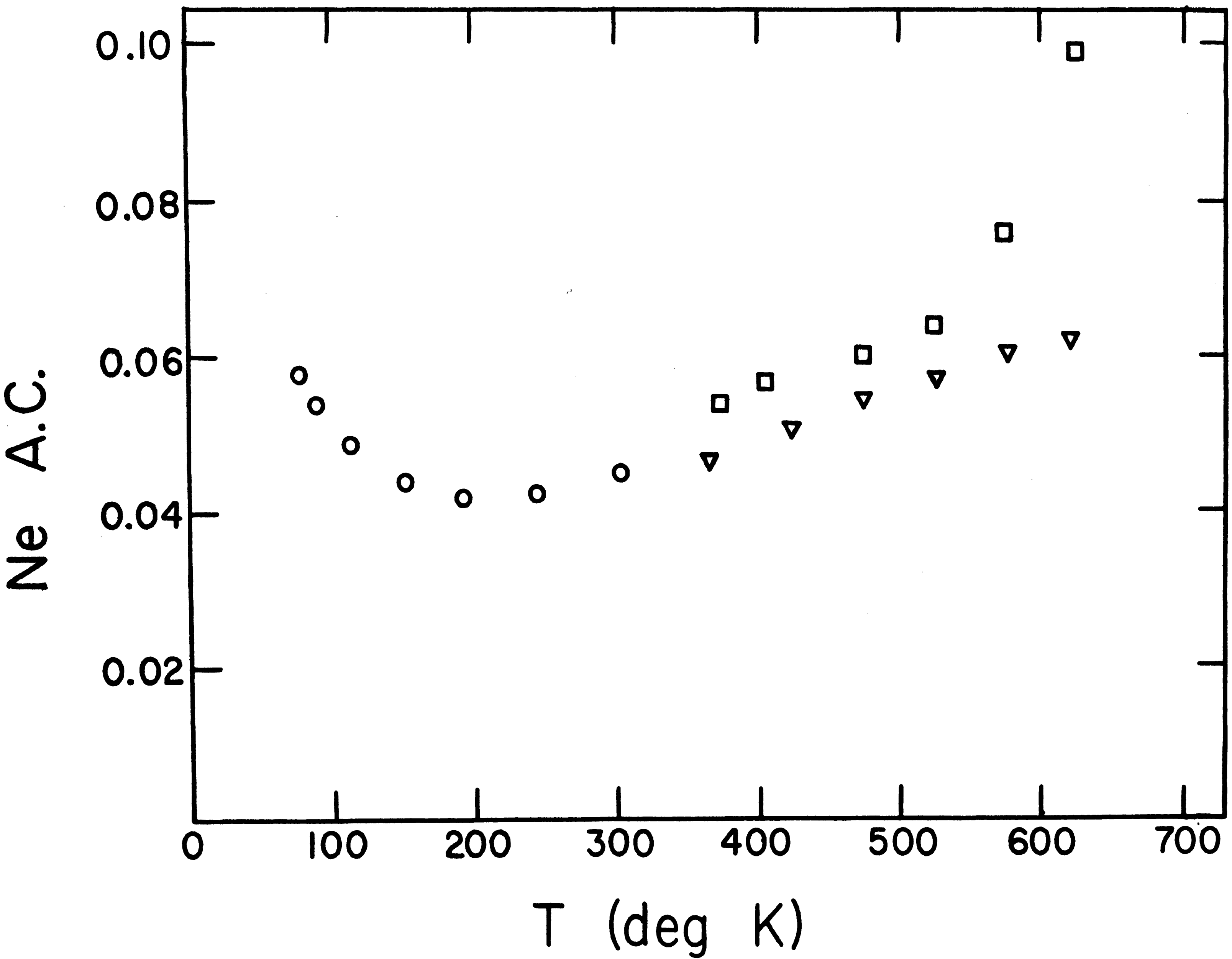


FIGURE 5

FIGURE 6

EXPERIMENTAL RESULTS FOR HELIUM COMPARED WITH THEORY

□	This work
——	Devonshire calculations with $\kappa = 1.3\ \text{Å}^{-1}$, $D = 320$ cal mole^{-1}
· · · · ·	Devonshire calculations with $\kappa = 1.3\ \text{Å}^{-1}$, $D = 190$ cal mole^{-1}
— — —	Goodman-Wachman calculations with $\kappa = 1.64\ \text{Å}^{-1}$, $D = 210$ cal mole^{-1}
- - - -	Trilling calculations with $\kappa = .60\ \text{Å}^{-1}$, $D = 110$ cal mole^{-1}

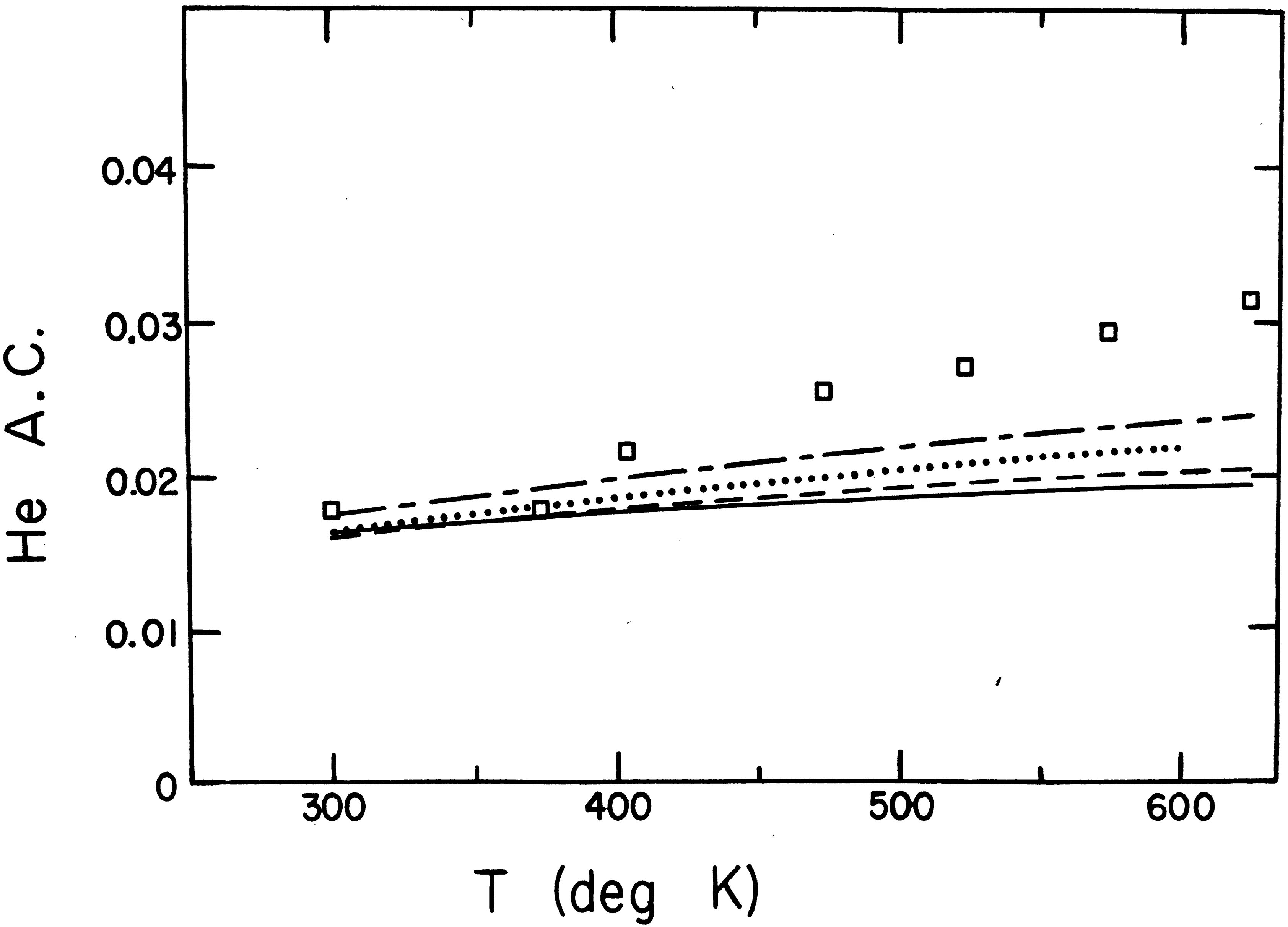


FIGURE 6

FIGURE 7

EXPERIMENTAL RESULTS FOR NEON COMPARED WITH THEORY

□ This work

—— Devonshire calculations with $\kappa = 1.7\ \text{Å}^{-1}$, $D = 500$ cal mole^{-1}

--- Goodman-Wachman calculations with $\kappa = 1\ 64\ \text{Å}^{-1}$, $D = 500$ cal mole^{-1}

----- Trilling calculations with $\kappa = .60\ \text{Å}^{-1}$, $D = 400$ cal mole^{-1}

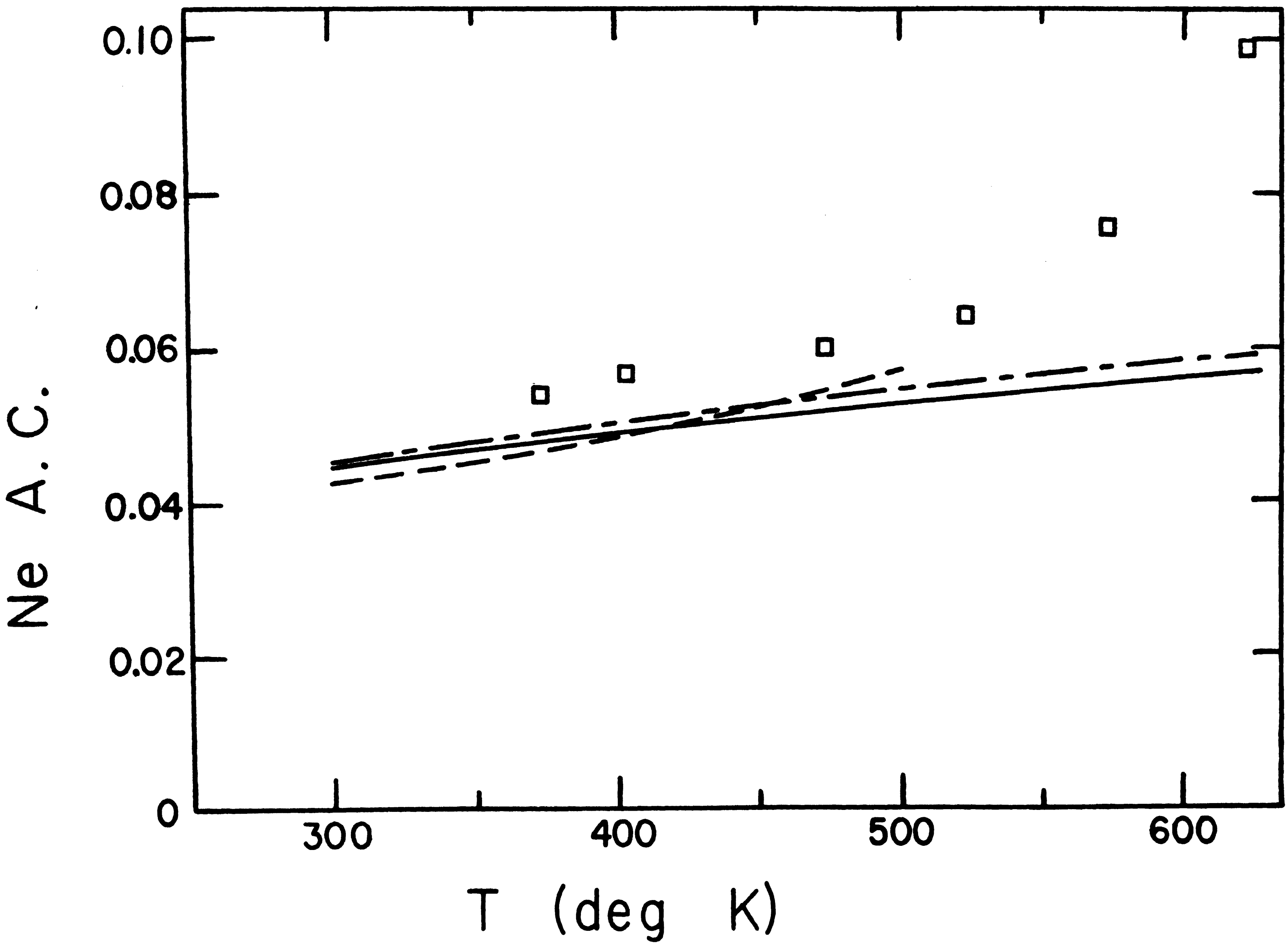


FIGURE 7

VITA

The author was born in Swedeborg, Missouri, April 26, 1943. His family moved to Springfield, Missouri, and he attended the public schools of that city. He entered Southwest Missouri State College in 1960 and received a B.A. degree in 1964. He worked from 1964 to 1966 as a chemical technician for Hoffman-Taff Inc. in Springfield, Missouri. He entered the graduate school of the University of Missouri at Rolla in 1966 and has been engaged in graduate study since that time. He is married and has two children.

Appendix A

A HISTORICAL REVIEW

Incomplete energy transfer between gases and solids was first observed by Kundt and Warburg (1) in 1875 when they noted that a vibrating disc was damped less than expected at low gas pressures. This phenomenon was in agreement with Poisson's prediction that a temperature discontinuity might exist between a body of gas and a wall if they were unequally heated. At Warburg's suggestion, Smoluchowski (2) carried out experiments to measure the heat conduction from the glass bulb of a thermometer by air and hydrogen at low pressures. He found that a temperature discontinuity did exist between the glass bulb and the gas around it, and that there was an incomplete energy transfer at the surface of the bulb.

In 1911 Soddy and Berry (3) and Knudsen (4) carried out experiments to determine heat conduction from a surface to a gas. Knudsen then defined a ratio expressing the efficiency of the energy transfer from the wall to the gas as the thermal accommodation coefficient (hereafter abbreviated as A. C.). This ratio is expressed as

$$\text{A.C.} = (E'_r - E'_i)/(E'_s - E'_i)$$

where E'_i is the average energy of a stream of atoms incident to the surface, E'_r is the average energy of the stream of atoms leaving the surface, and E'_s is the average energy of a stream of atoms leaving the surface at the temperature of the surface. E'_r must be equal to or less than E'_s, thus the A. C. will be between the values of zero and one.

Experimental Determinations of the A. C.

There are several methods for determination of heat conduction by a gas from a surface. These methods, reviewed by Kennard (5), depend on the geometrical configuration of the conductivity cell as well as the mean free path of the gas molecules relative to the dimensions of the conductivity cell. Most reliable A. C. determinations have been made using the low pressure method suggested by Knudsen. This method utilizes the coaxial cylinder geometrical arrangement, where the radius of the inner cylinder is much smaller than both the radius of the outer cylinder and the mean free path of the gas atoms. With this arrangement the temperature of the gas impinging on the surface of the filament is essentially the same as that of the walls of the outer cylinder. By thermostating the walls of the outer cylinder at a given temperature, T_w, the temperature of the gas can be known accurately as T_w. A knowledge of the temperature of the gas permits the calculation of the average energy of the monatomic gas molecules striking the filament, i. e., $2kT_w$, where k is the Boltzmann constant. If the monatomic gas comes to thermal equilibrium with the surface of the filament, the average energy of the monatomic gas stream leaving the surface will be $2kT_s$, where T_s is the temperature of the surface. From kinetic theory the number of collisions with the surface per unit area per unit time is given by $P/(2\pi mkT_w)^{1/2}$, where m is the mass of the gas molecule, thus the maximum amount of energy that can be transferred from the surface per unit time is $2k(T_s - T_w)P\sigma/(2\pi mkT_w)^{1/2}$, where σ is the surface area. The energy per unit time transferred from the surface to the gas can be measured electrically by measuring the power transferred from the filament under evacuated conditions, P_v, and subtracting that from the power, P_g, lost from the filament when the gas is present. Then the A. C. will be given as

$$\text{A. C.} = \frac{(P_g - P_v)(2\pi mkT_w)^{1/2}}{2k(T_s - T_w)P\sigma}$$

in terms of power.

There are two major problems in the determination of the thermal A. C. The first is determination of the surface area of the solid. The second is the maintenance of a well-defined surface. The surface area of the filament is determined from the dimensions of the filament, assuming that the filament is a cylinder. This assumption can lead to errors as the surface of the filament is not molecularly flat. Attempts to calculate surface roughness have been made by Roberts (6) and Langmuir (7), although the value of these corrections is uncertain. To maintain a well-defined clean surface, ultrahigh vacuum techniques must be employed to eliminate recontamination of the cleaned surface.

Between the time that Knudsen defined the A. C. and the time when Roberts (6) attempted to determine the A. C. of helium on nickel and tungsten in 1930, little work of importance on the subject was accomplished. Roberts used high vacuum techniques to evacuate his apparatus, and then circulated the helium in the apparatus through charcoal traps immersed in liquid nitrogen to remove impurities from the helium. The tungsten filament was flashed prior to each experiment at a temperature of 2000°C to clean the surface. The A. C. was measured as a function of time and extrapolated to zero time to obtain the value of the A. C. of helium on tungsten. The values obtained by Roberts were significantly lower than any previously measured and represented the first serious attempt to measure A. C. s on well-defined surfaces.

Although other A. C. measurements were reported between the 1930's and 1950, the next major experimental attempts to make A. C. measurements on well-defined surfaces were due to Thomas and coworkers. Over the last twenty years, Thomas et al. have investigated many gas-solid combinations (8-18), however, only those measurements of particular relevance to the work reported here will be described.

In 1955 Thomas and Schofield (10) published A. C. data for helium on tungsten from 77°K to 303°K having used a gettered system. These values were the lowest yet obtained, did not change with time, and were very reproducible. Thomas (8) and Silvernail (11) have reported reliable values for the A. C. of all the noble gases on tungsten, obtained in the same manner as the previous helium data. More recently, Thomas (19) and Krueger (18) have presented reliable A. C. data on the ratio of helium 4 to helium 3 on a tungsten surface from 77°K to 513°K as a test for theoretical A. C. calculations. These results of Thomas et al. form the principal body of reliable experimental data and are invaluable for examination of the thermal accommodation process from a theoretical viewpoint.

Menzel (20), in 1967, reported A. C. data for the noble gases on tungsten and molybdenum at 77°K and 300°K. He also reported the values of these A. C. s as a function of the temperature difference between the gas and the solid. All of these values were in agreement with those reported by Thomas.

Theoretical Evaluation of the A. C.

The earliest attempt at theoretical calculation of A. C. was made in 1914 by Baule (21) who considered elastic collisions over all angles between two atoms and derived the equation

$$\text{A. C.} = \frac{2m_g M_s}{(m_g + M_s)^2}$$

where m_g was the mass of the gas atom and M_s was the mass of the surface atom. Later in 1935, Landau (22) derived a formula, using classical mechanics, by considering collisions of a gas atom with an elastic surface interacting through a repulsive potential which was expressed as

$$\text{A. C.} = \frac{6}{m_g^{1/2} M_s} \left(\frac{\pi \hbar^2 \kappa^2 T}{k \, \theta^2} \right)^{3/2}$$

M_s and m_g were the same as above, while $\hbar$ was Plank's constant, κ was the interaction parameter of the repulsive potential, k was the Boltzmann constant, θ was the characteristic temperature of the solid, and T was the temperature of the gas. This formula was an obvious improvement over the first in that it took into account the physical parameter of the surface as well as of the gas. However, the temperature dependence predicted by Landau was not that which actually occurred.

At this point it became evident that quantum mechanics could be applied to the theoretical calculation of A. C. Since then studies have been divided into two groups, those using a quantum mechanical approach versus those using a classical mechanical approach. Noteworthy, for the purposes of this thesis, are the quantum theories of Jackson and coworkers (23, 24, 25). These theories, developed in the 1930's, used a repulsive potential between the surface and the gas molecule and were later refined by Devonshire (26) in 1937. Devonshire considered a one-dimensional gas interacting normally to the surface through a Morse potential. For such a system the energy transferred to or from the surface was postulated to be dependent on the probability of transition of the surface vibrational states when interacting with a gas atom. The Devonshire theory has been the principal quantum mechanical theory for A. C. to date, although it has recently been modified by Goodman (27), Feuer and Allen (28), Roach and Harris (29), and Gadzuk (30). A useful review of these theories has recently been made by Goodman (31).

Among the numerous classical mechanical theories of thermal accommodation, of particular importance for the work described herein are results of Goodman (32), Trilling (33), Logan and Stickney (34), Goodman and Wachman (35), Rapp and coworkers (36, 37), Chambers and Kinzer (38), and Raff et al. (39). The various approaches vary accordingly with the choices of interaction potential (e.g. Morse versus Lennard-Jones 6-12), the model chosen to represent the surface (e.g. continuous elastic, vibrating cubes, vibrating spheres), and of course, the approximations utilized in the theories.

The theories, quantum mechanical or classical mechanical, yield expressions for the A.C. which generally depend on six parameters, namely m_g, M_s, T, θ as defined above, and interaction parameters for the potential (e.g. κ , and D for the Morse potential). For a given gas-solid system m_g, M_s, and θ are fixed and therefore at a given temperature the interaction parameters may be varied. Once the interaction parameters are determined, to give an A.C. which agrees with experimental values at one temperature, these values of the interaction parameters may be used to theoretically predict the temperature variation of the A.C. for comparison with experimental results. Thus it is of prime importance to have available data over as large a temperature range as possible for such tests of the various theories. The work reported in Part II was directed toward providing such data at high temperatures.

No previous attempts had been successful in extending A. C. determinations above $513^{o}K$ and therefore the present work represents a significant extension of available data.

Appendix B

DEVELOPMENT OF THE HIGH TEMPERATURE METHOD

An account will be given here of the development of the experimental thermal conductivity cell in order that the reader might understand the difficulties involved in this research. Some ideas for further perfection of the experimental cell will also be given.

Accommodation coefficient measurements as a function of temperature have been limited to a maximum temperature of 513°K due to the use of pyrex glass conductivity cell. Above this point, the glass outgasses water which in turn contaminates the measurement surface. In order to eliminate this problem, a thermal conductivity cell of molybdenum was employed, heated by radiation from heating filaments located symmetrically around it and encased in a cooled glass envelope. The glass envelope could be maintained at 26°C while the inner conductivity cell operated at elevated temperatures without contamination of the filament. To check the feasibility of this arrangement a molybdenum sheet was heated in a vacuum by two heating filaments to a maximum of 400°C. The ability of the molybdenum to be heated to such temperatures gave sufficient encouragement for proceeding with this method.

The first experimental cell constructed consisted of a 15 cm molybdenum cylinder 20 mm in diameter suspended in a cylindrical vycor glass vacuum envelope. Heating filaments were located symmetrically around the molybdenum cylinder and one thermocouple was used to monitor the temperature of the cylinder. A filament 1 mil in diameter and 40 cm in length was connected to the leads at the top and bottom of the vacuum envelope and passed coaxially through the molybdenum cylinder. A spring on the bottom lead to the filament was used to keep the filament taut. Potential leads were taken from a 10 cm portion of the filament inside the cylinder in order to make measurements on the filament.

This arrangement of the experimental cell was very fragile and after a short period of use the potential leads became hopelessly entangled with the filament, making measurements impossible. It was also impossible to correct for the difference in the temperature gradient over the filament between evacuated conditions and those when gas was present, therefore, this filament arrangement was discarded.

The second and third experimental cells were both essentially the same as the first with the exception of the filament arrangement. No information was obtained from the second cell. The lead arrangement for the second and third cells consisted of two long nickel leads extending into the molybdenum cylinder with a thermocouple attached to each lead to monitor its temperature. The measurement filament was welded to these two leads. With this arrangement it was found that the leads were at a lower temperature than the cylinder walls when the cylinder was being heated by the heating filaments, thus making accurate A. C. determination impossible.

The design of the fourth cell was altered extensively. The filament leads were attached directly to the molybdenum cylinder with the top lead attached through a pyrex glass bead. It was hoped that the glass bead would outgas sufficiently at 1100°C to enable measurements of the A. C. up to 700°K or 800°K without the problem of outgassing at these temperatures. A pyrex glass vacuum envelope was used for this cell which made possible a reduction in the total length of the experimental cell of about three inches by eliminating the necessity for the vycor to pyrex graded seal. The problem encountered with this cell was the inability to calibrate the resistance of the measurement filament at what was thought to be known temperature. Again the temperatures of the leads and the cylinder were different, which ruled out the possibility of making accurate A. C. measurements at higher temperatures as planned.

The molybdenum cylinder was lengthened to 24 cm in the fifth experimental cell. Heaters could be added to the leads to maintain the temperature of the leads with that of the cylinder, and the length of the measurement filament could be extended to 16 cm. Thermocouples were attached to the leads and to the cylinder. The ability to monitor the temperature of the leads as well as to heat them made it possible to maintain the leads and the cylinder walls at the same temperature. Accommodation coefficient determinations could be made up to 200°C with this added control. There was still some temperature discrepancy between the filament and the cylinder walls, however, it varied proportionately with the gas pressure and could be eliminated by applying the proper corrections. Before all the measurements with this cell were completed, one of the fragile heating filament metal to glass leads was broken while the cell was immersed in the transformer oil bath and the cell filled with oil.

Radiation shields were added to the top and bottom of the molybdenum cylinder on the sixth experimental cell while the rest of the construction was identical to that of the fifth cell. These shields decreased the error in the temperature of the filament by a factor of three, thus indicating that the reason for the temperature discrepancy was direct and indirect radiation from the heating filaments. Accommodation coefficients were determined using this cell to a temperature of 200°C. Due to mechanical failures this cell was unable to be utilized fully.

The seventh and final experimental cell, i. e. the one described in the experimental section of Part II, was only slightly altered by the replacement of glass sleeves on the lead heaters and the glass connecting bead with ones of quartz. In addition, the external electrical connections to the heating filaments were constructed with thermal expansion loops to remove tension from the metal to glass leads to the heating filaments. This cell performed very well.

For the extension of these determinations it is recommended that other thermal conductivity cells of this type should have a cylindrical radiation reflector around the heating filaments, between them and the vacuum walls. This would enable the inner molybdenum cylinder to be heated to the desired temperature with less temperature difference between it and the heating filaments. The effect of this would be to reduce the stray radiation in the experimental cell and, consequently, reduce the heating effect on the central filament. One problem which might occur is that of radiation escaping the ends of the cylinder from the central filament which could cause the central filament to be at a lower temperature than the walls of the molybdenum cylinder.

To extend the determinations beyond 623°K a ceramic material of some kind must be used for the lead heaters and upper lead connection because quartz outgasses water vapor above that temperature and contaminates the measurement filaments surface. This ceramic material must be completely outgassed at high temperatures so that it will not outgas at the temperature at which the A. C. will be determined.

Appendix C

JUSTIFICATION OF THE METHOD OF EXTRAPOLATION OF APPARENT A. C. TO OBTAIN CORRECT A. C.

A plot of the apparent A. C. versus the inverse of ΔT must be shown to be linear if the method of extrapolation of the apparent A. C. to the zero of the inverse of ΔT is to yield a correct A. C. An initial assumption must be made that the correct A. C. is constant with ΔT. This assumption, particularly for helium and neon on tungsten, is supported experimentally by Thomas (10) and Menzel (20), and theoretically by the Devonshire theory.

The equation for calculating the A. C. is expressed as

$$\text{A. C.} = \frac{(2\pi m k T_w)^{1/2}\,(P_g - P_v)}{2kP\sigma\,(T_s - T_w)} \tag{I}$$

where P_g is the power loss in the gas, P_v is the power loss in vacuum, k is Boltzmann's constant, T_w is the temperature of the walls, T_s is the temperature of the surface of the filament, P is the gas pressure, m is the mass of the gas atom and σ is the surface area of the filament.

For constant pressure, P, and constant wall temperature, T_w, Equation I can be simplified as

$$\text{A. C.} = K\,\frac{P_g - P_v}{\Delta T} \tag{II}$$

where $K = (2\pi m k T_w)^{1/2}/(2kP\sigma)$ and $\Delta T = (T_s - T_w)$.

If, as in the present case, there is a negative error in the ΔT, ΔT_e, or a negative error in $P_g - P_v$, P_e, then the apparent A. C. is expressed by the following relationship:

$$\text{A. C. app.} = K \frac{(P_g - P_v - P_e)}{(\Delta T - \Delta T_e)}$$

where P_e and ΔT_e are constant for a given T_w and gas pressure. In order to plot A. C. app. versus the inverse of $(\Delta T - \Delta T_e)$ and extrapolate to the correct value of the A. C. as the inverse of $(\Delta T - \Delta T_e)$ goes to zero it must be shown that

$$d\,[\text{A. C. app.}]\,/d[1/(\Delta T - \Delta T_e)] \text{ is the constant.}$$

This can be shown if it is assumed that the A. C. is constant with respect to ΔT.

From Equation II

$$P_g - P_v = \text{A. C.}\,\Delta T/K$$

then

$$\text{A. C. app.} = K \left\{[\Delta T\,(\text{A. C.})/K] - P_e\right\} /(\Delta T - \Delta T_e) \qquad \text{(III)}$$

and

$$d\,[\text{A. C. app.}]\,/d\,[1/(\Delta T - \Delta T_e)] = -KP_e + \text{A. C.}\ \Delta T_e. \qquad \text{(IV)}$$

Therefore, the slope of the line is constant since K, P_e, A. C., and ΔT_e are constant under the conditions for the measurements.

As ΔT becomes large with respect to ΔT_e, so will $P_g - P_v$ become large with respect to P_e, and ΔT_e and P_e will become negligible. Then Equation III reduces to

$$\text{A. C. app.} \approx K \frac{[\Delta T\ (\text{A. C.})]}{K \Delta T}$$

and

$$\text{A. C. app.} \approx \text{A. C. at large } \Delta T.$$

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