[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MISSOURI]

The Accommodation Coefficients of He, Ne, A, H_2, D_2, O_2, CO_2, and Hg on Platinum as a Function of Temperature

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Introduction

When one attempts to apply the Pirani type pressure gage to the problem of following quantitatively the course of a reaction involving gases at low pressure, he must have at hand a knowledge of the free molecule heat conductivity for each gas, consumed or produced in the reaction, from the particular filament surface used in the gage. This low pressure heat conductivity may be most conveniently expressed as the product of the theoretical heat conductivity (involving the heat capacity, molecular weight and temperature of each gas) and the accommodation coefficient of each gas upon the particular filament surface material. This latter expresses the average temperature increment of the gas molecules, after engagement with the surface, as a fraction of the temperature difference between the filament and the incident molecules. Upon examination of values of the accommodation coefficients of various gases on platinum available in the literature it was evident that the values were not consistent enough among the various investigators to be usable with any degree of certainty. The available values are listed and discussed later in the paper. We have found, aside from a number of isolated measurements on one or two gases, but two sets of accommodation coefficient measurements on a sizable number of gases on platinum in the low pressure range and these date from 1910 and 1915 before modern vacuum technique was available. The relative values of accommodation coefficients of these sets of gases determined on the same filament should be more significant than isolated values. Also, from the standpoint of application to the Pirani gage, the few investigations in which the coefficients were determined at a series of temperatures show a considerable variation of the values with temperature so one could not use values of coefficients at temperatures other than those at which they are determined. The original immediate purpose of this work was to obtain values of the coefficients which would be applicable over the temperature range convenient for operation of the Pirani gage but, during the course of the work, this purpose became extended somewhat.

We have described in a preceding paper[1] an apparatus similar to that used by other investigators for measuring accommodation coefficients and applied it to a determination for mercury vapor on platinum. We have since applied this apparatus, involving 0.0025-cm. potential leads on a 0.01-cm. main filament, in a preliminary set of measurements of the accommodation coefficients of hydrogen, helium, oxygen and argon in a pressure range of 0.01 to 0.05 mm. The results are described below with reference to the corresponding curves of Fig. 4. The curves for hydrogen and helium meet those of Fig. 4 tangentially in the region of $\Delta T = 300°$, are concave upward, and have intercepts on the $\Delta T = 0$ axis about 40% higher than those of Fig. 4. The curves for oxygen and argon meet those of Fig. 4 in the region of $\Delta T = 300°$, are concave upward, and would give extrapolated intercepts at $\Delta T = 0$ of approximately unity. Although the difficulty of obtaining consistent values of the accommodation coefficient increases as ΔT becomes smaller, repeated attempts were made to approach the limiting value as $\Delta T \rightarrow 0$ with results consistently suggesting a value of unity for argon and oxygen. The truth of this result, of course, was doubted; so a detailed consideration of errors in the method was undertaken, especially errors due to the temperature distribution in the filament and leads. These considerations are outlined below since they apply to apparatus of other investigators and since they show the need for the condition of uniform temperature throughout the filament which it is hoped is achieved by the apparatus described subsequently.

The following differential equation, which approximately represents the heat produced electrically and the heat gained or lost by metallic conduction along the filament, the heat radiated from the surface, and heat conducted by the gas from the surface for an infinitesimal segment of the filament, was set up and integrated.

$$K_{\text{Pt}} \frac{\pi d^2}{4} \frac{d^2T}{dx^2} = -\frac{\pi d^2}{4} I^2 R_{T_\text{w}} [1 + k(T_\text{f} - T_\text{w})] + \pi d e \sigma (T_\text{f}^4 - T_\text{w}^4) + \pi d a \Lambda_\text{p} (T_\text{f} - T_\text{w})$$

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(1) Thomas and Olmer, THIS JOURNAL, **64**, 2190 (1942).

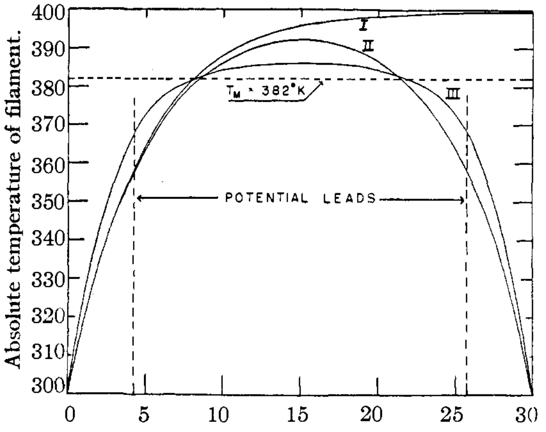

Fig. 1.—Temperature distribution over: I, end of long 0.01 cm. platinum filament in vacuum; II, 30 cm. of 0.01 cm. platinum filament in vacuum; and III, 30 cm. of 0.01 cm. platinum filament in 0.02 mm. of argon at the same average temperature between potential leads as in II.

The second integration, performed graphically, gives the temperature of the filament as a function of x, the distance from the end. "K"$_{\text{Pt}}$ is the heat conductivity of platinum; "d" is the diameter of the filament; "x" is the distance from an end of the very long filament; "I" is the current; "R_{T_w}" is the specific resistance of the platinum at the temperature of the wall, "T_w"; "k" is the appropriate temperature coefficient of resistance based on R_{T_w}; "T_f" is the absolute temperature of the filament at x; "e" is the emissivity of platinum; "σ" is the Stefan–Boltzmann constant; "a" is the accommodation coefficient; "Λ" is the theoretical free molecule heat conductivity of the gas per unit pressure; and "p" is the pressure of gas in contact with the filament. For a more accurate representation one should express "K_{Pt}," "e" and "a" as functions of the temperature. In this calculation the values of these at the maximum temperature of the filament were used. The results of the calculations are shown in Fig. 1. Curve I represents the temperature distribution for 30 cm. at the end of a very long filament of 0.01-cm. platinum in vacuum heated with a current which would produce a maximum temperature of 400° K. at a great distance from the end with the wall at 300° K. Curve II represents an estimate based on Curve I of the distribution over a 30-cm. filament, as used in our apparatus, when both ends are at 300° K. and the current is sufficient to bring the middle portion of a very long filament to 400° K. The maximum temperature of this filament is about 392° K. The temperature of the filament measured in the accommodation coefficient experiments is the average between the potential leads, which are 4.25 cm. from the ends as shown by the vertical broken lines, and appears to be 382° K. The method of obtaining accommodation coefficients with this type of apparatus is to set the filament at the desired average temperature between the leads, measure the power loss in vacuum, add known gas pressures, then readjust the current until the average temperature between the leads is brought to the original value. The difference in power expenditure from the filament between the leads in gas and vacuum is assumed to be that conducted by the gas and the accommodation coefficient is calculated from this difference. Curve III is the temperature distribution over the filament with 0.02 mm. of argon, or its equivalent in heat conduction, with such a current that the average temperature between the leads is the same as for Curve II. It is noted, as one would expect, that the effect of adding gas is to flatten the curve in the central portion and raise the temperature at the potential leads, still neglecting the effect of conduction from the main filament by the potential leads. This changed distribution would give rise to two types of error—one type due to difference in temperature gradient in the main filament at the potential leads, hence a different amount of the electrical heat input being conducted out by the platinum in the cases in vacuum and in gas; the other type of error due to the new value of $e\sigma T_f^4$ averaged over the changed temperature distribution, hence an actual change in the radiation loss although the mean temperature is kept constant. The radiation loss in the case of argon at 0.02 mm. and average filament temperature of 382° K. is 27% of the total and with some of the experiments with mercury vapor was 97% at the highest mercury pressures used so a change in radiation loss with addition of gas will be carried over as an error in the accommodation coefficient and the magnitude of the relative error in accommodation coefficient will be greater or less than the relative change in radiation loss depending on whether the radiation loss is more or less, respectively, than the loss by gas conduction. In addition to the above calculation represented in Fig. 1, the temperature distributions along the 0.0025 cm. potential leads in vacuum and in 0.02 mm. of argon were calculated using an equation similar to the above but with no electric power supplied

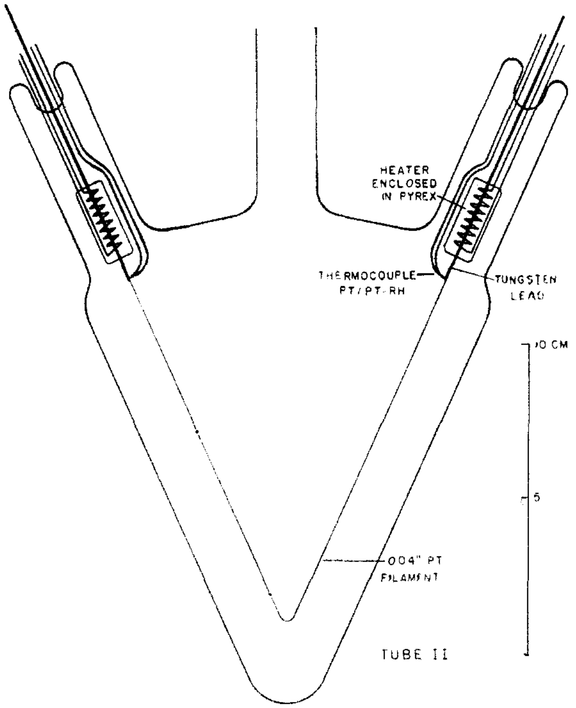

Fig. 2.—The tube for accommodation coefficient measurements.

The temperature gradient in the leads at the point of attachment to the main filament was found to increase from 18 deg./cm. in vacuum to 48 deg./cm. upon addition of the 0.02 mm. of argon. Even though the ratio of cross section of potential lead to filament, 0.06, was unusually favorable for this type of apparatus, this large change in temperature gradient would introduce an appreciable error in the accommodation coefficient of argon—about 3%. The total error from the three sources, considered independently, was estimated to make the value for the accommodation coefficient of argon about 6% too high. This type of apparatus may give reliable results in some ranges of pressure and temperature but certainly not in the ranges to be investigated in this work as shown by a sample calculation and as shown experimentally by comparison with the data of Fig. 4. With this type of apparatus one would have to apply corrections to obtain the objectives of this research and this would be a laborious process which could not be done accurately without a knowledge of the variation of the accommodation coefficient, emissivity, and heat conductivity of the filament material with temperature. If corrections must be applied it would be better to use a filament with no potential leads.

Experimental

Rather than proceed further with either of the above types of tubes and the necessary correction calculations an apparatus which, it is believed, practically eliminates end losses was designed and constructed and used to obtain the measurements presented in this paper. A diagram of the tube is shown in Fig. 2. The filament consists of 26 cm. of 0.01 cm. platinum (Bishop Co., c. p. grade) hung in a loop in a cone-shaped envelope (a 500-ml. Erlenmeyer with bottom rounded and neck sealed off). The filament is welded at each end to a very short piece of 0.05-cm. platinum which in turn is welded to a long lead of tungsten rod, 0.05 cm. in diameter. Heaters of fine platinum wire are fused into sleeves of Pyrex glass which are fused around the tungsten leads near the filament end. Thermocouples of platinum against platinum 90%-rhodium 10% are spot welded to the heavy platinum segments which hold the filament ends. The five lead wires are brought out through glass-metal seals. The platinum leads of the thermocouples serve also as potential leads for the resistance and power measurements. Temperature-e. m. f. calibration of the thermocouples and temperature-resistance calibration of the filament were carefully made. The method of operation of the tube is described below with reference to the electrical circuit shown diagrammatically in Fig. 3. The resistance of the filament corresponding to the desired operating temperature was set to the nearest 0.1 ohm on the dial box, R_2. The e. m. f. value for the thermocouples corresponding to this resistance value was determined from a large-scale graph and this was set on the millivolt potentiometer. Resistances R_3 and R_4 were then adjusted until the same e. m. f. value was obtained for the switch at the Type K_2 potentiometer thrown to R_2 and to the potential leads of the filament and until the current through the heaters brought the thermocouples to the predetermined e. m. f. The adjustments of R_3 and R_4 to the final values cannot be done independently. When the condition of balance obtains the filament must be at constant temperature over its entire length except for error in calibration and measurement of the temperature in terms of the filament resistance and the thermocouple

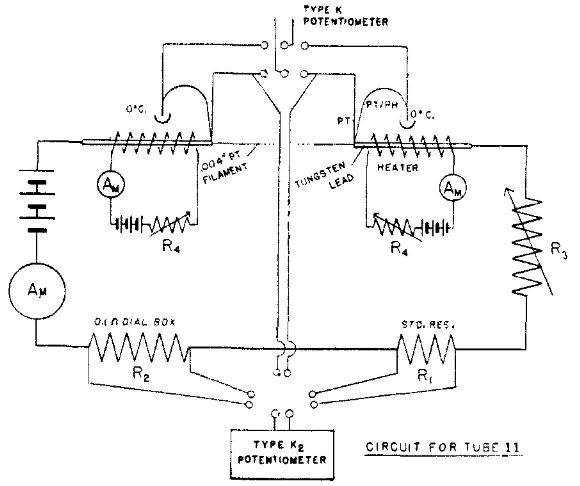

Fig. 3.—Electrical circuit for the tube.

e. m. f., and except for non-uniformity of wire cross section, and except for radiation and gas conduction effects on parts of the filament from the heaters and from other parts of the filament—all of which are quite small sources of error in the final accommodation coefficient. It is believed that this tube practically eliminates the necessity for end loss correction, probably more completely than the compensation method, using a long and short filament, unless the filaments are made longer than those described in the literature. The final resistance and current measurements were made with reference to the standard, R_1.

The tube was immersed in a thermostat bath held at 30.0° and was attached through a "U" tube to a high vacuum system with mercury condensation pump, McLeod gage calibrated with extreme care, mercury cut-offs, and no stopcocks or greased or waxed joints in the high vacuum line.

Runs were made in two ways with results in good agreement. In the first method the pressure of the gas under consideration was varied from zero to a maximum of 0.05 mm. and the filament and heaters brought to balance at the original temperature after each addition of gas. The power loss varied linearly with the pressure and the slope of the line gave the power loss per unit pressure which was used to determine the accommodation coefficient. For the second method the power loss in vacuum was measured with the tube brought to balance at a series of temperatures and a plot of power loss against filament resistance was made. The power loss of the filament in the presence of the gas under consideration at known pressure was then determined at a series of temperatures and plotted against filament resistance. The difference in ordinates of the curves with gas and in vacuum (power loss) at corresponding filament resistances (temperature) divided by the pressure used in obtaining the upper curve gives the same quantity as the slope of the lines mentioned in the first method and is used to calculate the accommodation coefficient. This quantity, which we call $\Delta W/p$, when divided by the surface of the filament in square centimeters, ΔT, and the proper conversion factor to make the dyne/cm.² the pressure unit, and then divided by the kinetic theory expression for the free molecule heat conductivity, Λ, which applies to an apparatus consisting of a small diameter filament losing heat in a large volume gives the accommodation coefficient, a. We have used

$$\Lambda = \frac{\rho\bar{c}}{4}\,\frac{Cv + {}^1/{}_2R}{M} = \left(\frac{Cv}{R} + {}^1/{}_2\right)\sqrt{\frac{R}{2\pi MT}}$$

in which ρ is the density, $\bar{c}$ the mean speed, C_v the molar heat capacity at constant volume, and M the molecular weight, all quantities referring to the gas at the temperature of the wall. The first method above is more reliable than the second but much more laborious. In the first method a set of power readings is taken at a number of pressures to get the accommodation coefficient at a single temperature while in the second method one has the accommodation coefficients over the whole temperature range when the run is completed. All runs with mercury vapor were made by the first method due to the small difference in power loss with vapor and without. For the rest of the gases most of the values were obtained by the second method with two or three check points obtained by the first method. Points by both methods are included in the plot of accommodation coefficients against ΔT, Fig. 4.

The hydrogen was introduced from a gas flame through a palladium tube. The deuterium was made by interaction of sodium with 99.5% deuterium oxide in a vessel attached to the low vacuum side of the system. The deuterium oxide was frozen down during evacuation, warmed up and allowed to react, then the remainder frozen down again. The low vacuum side was thoroughly flushed out with deuterium before letting the gas back through the condensation pump into the high vacuum system. Pure carbon dioxide was frozen down in a liquid air trap from which it was allowed to sublime into the low vacuum side and hence, with adequate flushing (as in all cases below) into the high vacuum system where it was frozen down repeatedly and opened to the pumps to free it from permanent gases. Oxygen was prepared from pure mercuric oxide and introduced through the low vacuum side. The inert gases were obtained from the Ohio Chemical Company in Pyrex flasks to each of which was joined a mercury seal stopcock followed by a standard slant-bore stopcock, leaving several cubic centimeters capacity between the stopcocks. The specified purities of 99.5% or better were accepted and these gases were introduced as described above through the low vacuum side of the apparatus. Liquid air was kept in the "U" tube connecting the filament containing tube to the high vacuum system for measurements on all gases except carbon dioxide and mercury. The carbon dioxide measurements were made in the presence of mercury vapor which was held constant by an ice-bath on the "U" tube. Measurements on carbon dioxide with dry-ice on the "U" tube were unsatisfactory due to the pressure instability of the carbon dioxide within the system. All gas pressures were read on the McLeod gage with the aid of a cathetometer to improve accuracy. Mercury pressure, of course, was established in equilibrium with liquid mercury and then corrected for thermal transpiration. "I. C. T." vapor pressure values were used.

Discussion

The measured accommodation coefficients are plotted in Fig. 4 and the estimated limiting values as $\Delta T \rightarrow 0$ at 30° are given in Table I in the column headed $\lim._{\Delta T \rightarrow 0}\, a$. The values of C_v/R used in the calculation of Λ are listed in the second column. Variation of C_v with temperature was neglected in the calculations. The theoretical free mole-

TABLE I

	$\lim._{\Delta T \rightarrow 0}\, a$	C_v/R	$\Lambda_{30° \text{C.}}$	$a\Lambda_{30° \text{C.}}$	$\frac{a\Lambda_{30}}{a\Lambda_{30(H_2)}}$
H_2	0.220	2.44	433.03	95.3	1
D_2	.295	2.44	306.31	90.4	0.948
He	.238	1.519	210.88	50.2	.527
Ne	.57	1.51	93.56	53.3	.56
A	.89	1.509	66.44	59.1	.62
Hg	1.00	1.50	29.52	29.5	.31
O_2	0.74	2.504	110.92	82.1	.86
CO_2	.76	3.38	122.31	93.0	.975
(CO)[a]	.75[a]	2.488	118.05	88.5[a]	.93[a]
(H_2O)[a]	.72[a]	3.30	187.31	134.8[a]	1.415[a]

[a] Estimated from values obtained with the first tube.

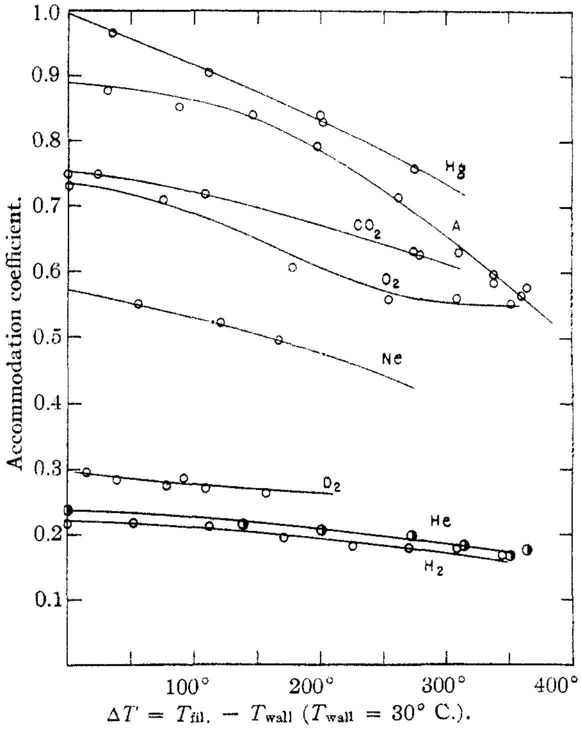

Fig. 4.—The accommodation coefficient measurements with the tube of Fig. 2.

cule heat conductivities in ergs per bar (dynes/sq. cm.) per square centimeter per degree temperature difference are listed for 30° in the third column. The actual heat conductivities from platinum in the same units, $a\,\Lambda_{30°}$, are given in the fourth column and the heat conductivities from platinum relative to hydrogen are given in the fifth column.

Comparison of the curves of Fig. 4 with those obtained with the earlier type of tube with potential leads and described earlier in this paper shows that the concavity to the upper right of those curves has disappeared with the new tube, which confirms the need for criticism of the first type of tube and which is in harmony with the conclusions drawn in the discussion relating to Fig. 1. The points of Fig. 4 fall in regular enough manner to permit reasonably certain extrapolation to $\Delta T = 0$. A number of the curves have points plotted at $\Delta T = 0$. These points were obtained by the second method of measurement described previously by making plots $\Delta W/P$ against ΔT and using the limiting slopes $\Delta W/P\Delta T$ as $\Delta T \rightarrow 0$ of these curves to calculate the accommodation coefficient at $\Delta T = 0$.

It seems of interest to consider the effect of molecular weight on the accommodation coefficient in a series of otherwise similar molecules. In the case of deuterium and hydrogen it is seen that the slower moving deuterium has enough larger accommodation coefficient almost to compensate for the greater speed and hence greater theoretical heat conductivity of hydrogen. If one makes the simple assumptions that, first, the rate of gain of energy of the molecule while in effective contact with the wire is proportional to the energy yet available from the wire and, second, the duration of effective contact with the surface is inversely proportional to the speed of the molecules, he calculates, using the value 0.220 for hydrogen, the value 0.296 for the accommodation coefficient of deuterium. The first assumption leads to $(E_0 - E)/E_0 = e^{-kt} = 1 - a$ in which E is the energy increment of the molecule in time of effective contact, t, and E_0 is the possible increment if temperature equilibrium between the filament and molecule were attained. The second assumption allows one to make kt for deuterium greater by $\sqrt{2}$ than for hydrogen. Similar calculations on the two other available sets of measurements on both hydrogen and deuterium[6,11] give values for deuterium approximately 3 and 4% higher than the observed. For the inert gases it is observed that the increasing accommodation coefficients from helium to argon over-compensate for the decreasing speeds, making argon a better heat conductor from platinum in the free molecule range than helium.

Below is a fairly complete list of the accommodation coefficient values obtained on platinum by various investigators for the gases reported in this paper. The pressure and temperature conditions of measurement are given with the references.

Two methods of determining accommodation coefficients, differing experimentally and in theory, are represented in the above table. References 2 to 9 inclusive use the low pressure heat conductivity method with pressure usually less than 0.05 mm. and references 10–14 use the high pressure heat conductivity method (1–100 cm.) and make use of temperature jump theory to obtain the accommodation coefficient. The mean of the seven values for hydrogen by the low pressure method is 0.254 with an average deviation of 0.054, while the four high pressure values average 0.285 with an average deviation of 0.029. For deuterium the single value by the high pressure method is 33% above the mean of the two by

TABLE II

H_2	0.22[2]	0.24[3]	0.36[4]	0.28[5]	0.20[6]	0.32[8]	0.183[9]	0.34[10]	0.29[11]	0.282[12]	0.23[13]
D_2	0.295[2]				0.263[6]				0.37[11]		
He	0.238[2]	0.38[3]		0.34[5]	0.245[6]	0.315	0.35[7]	0.41[8]	0.5[10]		
Ne	0.57[2]	0.75[3]		0.653[5]							
A	0.89[2]	0.80[3]		0.86[5]		0.63	0.748[7]		0.88[10]		
O_2	0.74[2]	0.62[3]	0.80[4]	0.84[5]					0.82[10]		
CO_2	0.76[2]	0.52[3]	0.86[4]	0.807[5]					0.78[10]	0.45[14]	

the low pressure method. For helium the single value by the high pressure method is 54% above the average of the seven of the low pressure method. The values for argon and oxygen are slightly higher for the high pressure method. We are inclined from several considerations to believe the values 0.52[3] and 0.45[14] for carbon dioxide to be in error. If so, the accommodation coefficient by the high pressure method for carbon dioxide is slightly less than the average of the others or just equal to the average of Knudsen's later value and our value. The apparent tendency for the values measured in the low pressure range to be less than those in the high pressure range appears reasonable because it seems well established[6,7,17] that in general the freer the surface from adsorbed gas the lower the accommodation coefficient. In view of the above it seems that the proposition of Gregory and Stephens[15] to obtain both the accommodation coefficient and C_v from a set of measurements in each of the pressure ranges may be a little over-optimistic in spite of the good C_v value they obtained for hydrogen.

The work presented in this paper approximately doubles the available data for accommodation coefficients on platinum as a function of temperature. We have plotted against absolute temperature in Fig. 5 the values of others on platinum (unbroken lines with points indicated) together with our own (unbroken lines with no points) and those of Keesom and Schmidt[16] on glass and Roberts[17] on scrupulously clean tungsten (broken lines). The accommodation coefficient measurements at low pressure may be divided into two classes: those using a filament which is allowed to become saturated (no change of accommodation coefficient with time) with the gas under consideration (or possibly in some cases with an impurity in the gas) and those in which, presumably at least, the measurements are taken on or may be extrapolated to values for a clean surface. The works of Mann[7] and Mann and Newell[6] are the only ones which attempt measurements of the latter type for platinum. The values obtained thus are much smaller than those on a saturated surface (see Mann's[7] curve for hydrogen, Fig. 5, lower right). The values in this paper, Fig. 4, were obtained on a filament which was frequently glowed in vacuum but then allowed plenty of time to become saturated with the gas present. Roberts'[17] measurements for helium on a clean tungsten surface (but not for neon, see Fig. 5, lower left) furnished the only case we have found which has the accommodation coefficient increasing with temperature below 500° K. although several cases show minima above 500° K. Eucken and Bertram[18] have shown that a number of gases condensable above 100° K. have accommodation coefficients on a rough oxidized nickel filament which approach unity as the temperature is lowered to the region of 150° K. Kistiakowsky, Lacher and Stitt[19] and Kistiakowsky and Nazmi[20] show that the ratios of

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(2) Thomas and Olmer, this paper: $T_f = 30°$ C.; $\Delta T = 0$; $p < 5 \times 10^{-2}$ mm.

(3) Soddy and Berry, *Proc. Roy. Soc.* (London), **A83**, 254 (1909); **A84**, 576 (1910); (values recalculated by Smoluchowski) $T_f = 60°$ C.; $\Delta T = 40°$; $p < 5 \times 10^{-2}$.

(4) Knudsen, *Ann. Physik*, **34**, 593 (1911); $T_f = 100°$ C.; $\Delta T = 80°$; $p \sim 2.5 \times 10^{-3}$ mm.

(5) Knudsen, *ibid.*, **46**, 641 (1915); T, ΔT, p unspecified (low pressure).

(6) Mann and Newell, *Proc. Roy. Soc.* (London), **A158**, 397 (1937); $T_f = 100°$ C.; $\Delta T = 84°$; (low pressure).

(7) Mann, *ibid.*, **A146**, 776 (1934); $T_f = 100°$ C.; $\Delta T = 84°$; $p < 0.37$ mm.

(8) Knudsen, *Ann. Physik*, **398**, 5F6, 129 (1930); $T_f < 100°$; $\Delta T = 20\text{–}80°$; $p < 0.02$ mm.

(9) Rowley and Bonhoeffer, *Z. physik. Chem.*, **B21**, 84 (1933) (recalculated according to our expression for Λ); $T_f = 20°$ C.; $\Delta T = 20°$; $p < 0.3$ mm.

(10) Dickins, *Proc. Roy. Soc.* (London), **A143**, 517 (1933); (values recalculated by Kennard, "Kinetic Theory of Gases," McGraw-Hill Book Co., New York, N. Y., 1938, p. 324) $T_f = 20°$ C.; $\Delta T = 20°$; $p = 1\text{–}10$ cm.

(11) Archer, *ibid.*, **A165**, 474 (1938); $T_f = 20°$ C.; $\Delta T = 20°$; $p = 10\text{–}100$ cm.

(12) Gregory, *ibid.*, **A149**, 35 (1935); $T_f = 30°$ C.; $\Delta T = 4°$; $p = 4\text{–}70$ cm.

(13) Gregory and Dock, *Phil. Mag.*, **25**, 129 (1938); $T_f = 15°$ C.; $\Delta T = 15°$; $p = 2\text{–}70$ cm.

(14) Archer, *ibid.*, **19**, 901 (1935); $T_f = 48°$ C.; $\Delta T = 8°$; $p = 1.5\text{–}50$ cm.

(15) Gregory and Stephens, *Nature*, **139**, 28 (1937).

(16) Keesom and Schmidt, *Physica*, **4**, 828 (1937).

(17) Roberts, *Proc. Roy. Soc.* (London), **142**, 519 (1933).

(18) Eucken and Bertram, *Z. physik. Chem.*, **B31**, 361 (1935).

(19) Kistiakowsky, Lacher and Stitt, *J. Chem. Phys.*, **7**, 289 (1939)

(20) Kistiakowsky and Nazmi, *ibid.*, **6**, 18 (1938).

accommodation coefficients of a number of gases, condensable at 88° K. or above, on bright platinum, platinum black and nickel oxide surfaces approach unity as the temperature is lowered toward 193° K. Perhaps the most illuminating measurements of accommodation coefficients as a function of temperature are those of Keesom and Schmidt[16] for helium, hydrogen, neon and nitrogen on glass down to 12° K. (see Fig. 5, broken curves). These authors suggest that the temperature at which the accommodation coefficient becomes unity is approximately the critical temperature and identify it with the temperature at which measurable adsorption begins to occur and they further state that they found no exception to this when applied to adsorption of the same gases on metals. From a consideration of the above it may be stated as a hypothesis with some support and no contradiction that: the accommodation coefficient of any gas from any surface saturated with the gas is unity below a certain temperature, departs from unity at this temperature, and decreases as the temperature rises. In certain cases at higher temperature, probably due to radical changes in the sorption process, the accommodation coefficient may pass a minimum value and rise again with increasing temperature. We hope soon, with some modification of the present apparatus, to extend the measurements over a wider temperature range, especially over the range of Keesom and Schmidt's for glass.

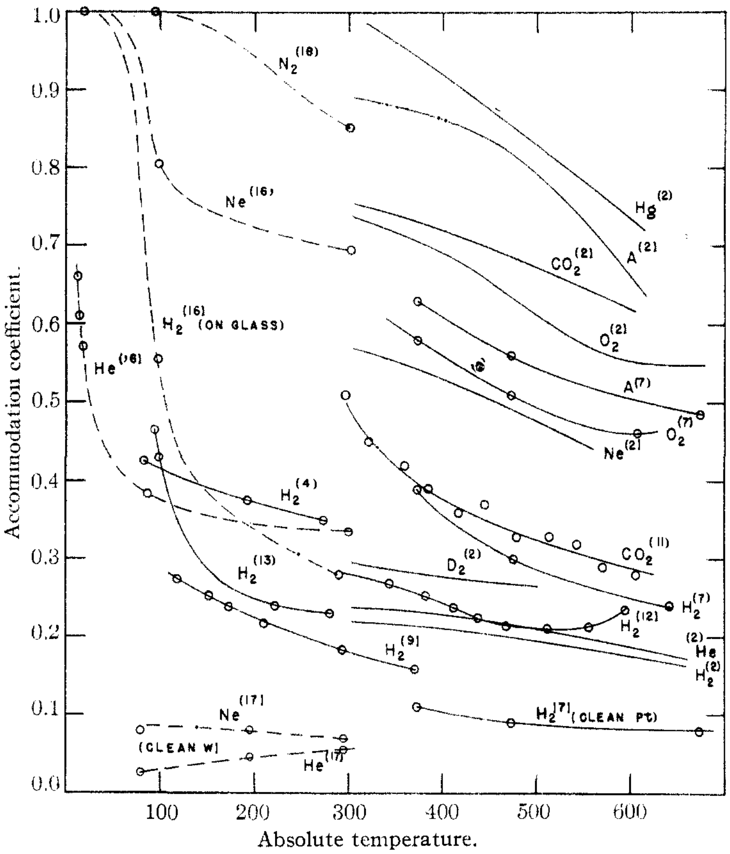

Fig. 5.—Measurements of accommodation coefficients as a function of temperature on platinum and other surfaces (broken lines) by various investigators.

Two authors[9,21] to our knowledge have defined the accommodation coefficient with the stipulation that $\Delta T \rightarrow 0$. In general this does not seem to be the sense in which it is defined, thereby implying that the value is independent of the ΔT at which it is measured and hence must depend on T_f alone. Below are several conflicting points of evidence on this matter which have come to our attention. Measurements which we have made with the earlier tube and in which T_f was held constant and T_w lowered indicated a decreasing accommodation coefficient with increasing ΔT but, due to uncertainties of end loss correction and thermal transpiration pressure correction, these were not considered conclusive. The detailed reports of a number of investigators (see for instance Keesom and Schmidt,[22] pp. 594, 595 and ref. 19, p. 292) show the quantity, power loss/ΔT, to fall off with unexpected sharpness for a small increase of ΔT—10% for some cases with an increase of ΔT of less than 30°—in temperature ranges where the change in accommodation coefficient measured at large ΔT would be small—not over 1% in the same 30° range. If experimental error can be discounted as an explanation of the above (the references cited appear to be among the most precisely done) it seems to us to throw evidence in support of a dependence of the accommodation coefficient on the ΔT at which it is measured. Our curve for mercury strikes us as giving evidence of the dependence of the accommodation coefficient on ΔT. The boiling point and critical point of mercury are so high

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(21) Jackson and Howarth, *Proc. Roy. Soc.* (London), **A142**, 447 (1933).

(22) Keesom and Schmidt, *Physica*, **3**, 590 (1936).

that it is improbable that our $\Delta T = 0$ or 30° would be the unique temperature at which $a = 1$ for mercury atoms. It would be our guess that a determination for mercury with T_w at a higher setting than 30° would likewise give $a \rightarrow 1$ as $\Delta T \rightarrow 0$. Evidence for the independence of "a" on ΔT is the curve for hydrogen of Rowley and Bonhoeffer[9] (partially plotted in Fig. 5). T_f is allowed to go from 109° K. to above 400° K. with the wall at 88° K. for T_f to 200° K., wall at 193° K. for T_f from 200° K. to 300° K., and wall at 273° K. for T_f above 300° K. No breaks occur in the curve between the points where T_w is shifted much nearer to T_f.

It is quite evident that much more experimental work, carefully controlled with respect to filament surface condition, purity of gases, and accuracy of measurement, must be done before knowledge of the quantitative behavior of the accommodation coefficient is satisfactory. The theory of accommodation coefficients on saturated surfaces is no doubt closely tied to adsorption theory and may in some cases involve primarily interaction of gas molecules with like molecules in an adsorbed condition rather than with the surface of the solid itself. This would lead one to suspect that the addition of the "$a\Lambda$" terms of Table I to get the total heat conductivity for mixtures of gases at low pressure would not be permissible unless proved so experimentally. Preferential adsorption of the molecules of one gas could well alter the accommodation coefficients of the other gases. We would hazard the opinion that with further development the study of accommodation coefficients may have considerable potentiality as a means of expanding the present knowledge of the field concerned with adsorption of gases on solids.

Summary

The temperature distributions over an electrically heated filament in vacuum and in gas are discussed and reasons for the desirability of having uniform temperature throughout the length of the filament for accommodation coefficient measurements are pointed out. A tube designed to give this condition is described and accommodation coefficients for eight gases obtained with this tube over a range of temperature are reported and compared with existing values.

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The Solubility of Hydrogen at Low Pressure in Iron, Nickel and Certain Steels at 400 to 600°

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Although several investigators have measured the solubility of hydrogen at 1 atmosphere pressure in various samples of iron and steel, there is considerable discrepancy between their results, particularly at the lower temperatures, probably because of the small magnitude of the solubility and the lack of consistency of the method used. There was, however, no information on the solubility at low partial pressures, such as are much more likely to be met with in practice, and little on how the solubility in steel is influenced by changes in composition of the steel. Accordingly, the measurements, described in this paper, at a hydrogen pressure ranging from about 0.001 mm. to 1.5 mm., on substantially pure iron and nickel, and on a number of steels at the temperature levels 400, 500, 600° were undertaken; on iron at 600° the pressure range was extended subsequently up to 350 mm. At each temperature, the measured solubility s is accurately represented, within the experimental error, by the linear equation $s/p^{1/2} = \alpha$, p being the pressure of hydrogen; and the values at all three temperatures are reproduced by the linear relation $\log(s/p^{1/2}) = A/T + B$. Extrapolation by means of this expression to a pressure of 1 atmosphere yields values in excellent accord with the mean data of previous investigators, at temperatures up to 900°. The results show that, within the range of pressure and at the three temperature levels investigated, the solubility in a ferritic steel does not differ greatly from that in pure iron; whereas in an austenitic steel the solubility is four or five times as great, and about the same as in pure nickel. There are, however, individual differences, which are quite reproducible, between steels; these seem to be due to differences in content of non-metallic elements, other than carbon, rather than of metallic elements.