[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Thermal Accommodation Coefficients on Gas-covered Tungsten, Nickel and Platinum[1]

By I. Amdur[2] and L. A. Guildner[3]

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Thermal accommodation coefficients of H_2, D_2, He, Ne, N_2, O_2, A, Kr and Xe on gas-covered W, Ni and Pt were determined at 9, 50 and 100°. For each gas, measurements were made simultaneously on the three wires under identical conditions of temperature, pressure and extent of surface coverage. Experimental procedures were carefully planned and controlled to permit retention of the maximum possible coverage of the wires by an adsorbed layer of air, assignment of non-ambiguous temperatures to the measured accommodation coefficients, and accurate analysis of the experimental results, particularly with respect to the effects of molecular collisions in the region of pressure usually assumed to be characterized by "free-molecule" conduction. The numerical results, supported by electron photomicrographs of the three wires, show that adsorbed gas layers of the present type completely mask the character of an underlying, smooth substrate, and that under such conditions the accommodation coefficients are virtually independent of the substrate. Between 9 and 100°, the accommodation coefficients on Ni and Pt showed a small decrease with increasing temperature which is attributed to slight desorption of the air layer. In the case of tungsten, which is known to have extremely strong adsorption properties, essentially no temperature dependence was observed. The accommodation coefficients were found to be independent of pressure over the range 0.004 to 0.3 mm. It is suggested that this is due to the particular experimental procedures which tended to preserve the character of the adsorbed air layer. The present results are compared with those of several earlier investigations in which partial studies of the present type have been made. Good agreement is found in those cases where sufficiently similar experimental conditions and procedures permit comparison.

Introduction

The thermal accommodation coefficient, which characterizes the heat conducted by a gas at relatively low pressures, has been the subject of many investigations. Critical examination of the literature indicates that the numerous discrepancies in the reported values may, in many instances, be traced to the very strong dependence of the accommodation coefficient on experimental conditions.

Previous determinations may be divided into three groups, as follows:

The first group consists of experiments in which the relevant surfaces have maximum gas coverage at the existing temperature, independent of pressure. This is accomplished by deliberately avoiding excessive heating of the surfaces which, therefore, retain an adsorbed gas layer, usually air, which was originally laid down at atmospheric pressure. This layer remains substantially intact under the mild vacuum treatment which is commonly used in such experiments. Measurements on these saturated, gas-covered substrates have been made at low pressures,[4–19] in the general region of the free-molecule conduction, and at higher pressures,[20–27] where the coefficient is deduced from the magnitude of the temperature-jump associated with thermal conductivity.

The second group involves essentially bare substrates,[12,28–31] usually wires which have been flashed to very high temperatures to remove previously adsorbed gas. In effect, the measurement of the accommodation coefficient is then completed before sufficient time has elapsed for appreciable gas coverage to be established at the existing pressures, which are in the free-molecule range.

The third group involves partially saturated substrates.[6,12,28–30,32–38] In general, these are flashed wires which have remained in contact with the gas whose accommodation coefficient is being measured for sufficient time to acquire equilibrium

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(2) John Simon Guggenheim Memorial Foundation Fellow at the Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California.

(3) E. I. du Pont de Nemours & Company Fellow, 1952–1953.

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coverage at the existing low (free-molecule region) pressure.

In many cases, the effects of the extent of gas coverage have not been clearly recognized. Consequently, results have been reported whose discordance frequently can be traced to lack of control of this important experimental parameter. In addition, measurements of accommodation coefficients in all three groups have been made over a wide range of temperature differences between the substrate and the surroundings (at ambient temperature). This, too, has introduced confusion into the results, since the accommodation coefficient depends upon both the ambient temperature and the temperature excess of the substrate above the ambient temperature. In fact, the value of the coefficient at a specified ambient temperature should, strictly, be that value obtained in the limit of zero temperature difference between the substrate and the surroundings. Finally, the effect of pressure on the accommodation coefficient seems to require clarification. Von Ubisch[17] assumes that there is no pressure dependence in his treatment of heat conduction in the pressure region where both free-molecule (molecular) and collisional (molar) transport must be considered. Thomas and Olmer[32] report no effect of pressure for wires which were flashed and subsequently partially covered with adsorbed gas. On the other hand, Spivak[12] implies a pressure dependence since he reports a dependence of the accommodation coefficient on the extent of surface coverage at constant temperature. Amdur, Jones and Pearlman[13] report a decrease of the accommodation coefficient with decreasing pressure which they attribute to partial removal of adsorbed gas from their unflashed substrate. Gregory and Sherif[16] have confirmed the findings of Amdur, Jones and Pearlman.

The relatively large amount of conflicting information concerning accommodation coefficients which exists in the literature may be explained only partially in terms of the effects discussed above. In some cases it is not possible to analyze the heat flow problem for the existing experimental conditions with sufficient precision to obtain reliable values of the coefficients. Even when this situation does not obtain, in some low pressure experiments the very small quantities of energy involved have not been measured with sufficient accuracy to permit satisfactory evaluation of the small difference (energy conducted by the gas) between the total energy input and the energy lost by radiation and end loss. At higher pressures, on the other hand, the second-order nature of the temperature-jump effect may be responsible for certain disagreements between accommodation coefficients obtained in this manner and those derived from low pressure measurements. For example, the small pressure dependence of the apparent thermal conductivity which is usually attributed to the effects of temperature jump may in part be due to a real pressure variation of the true thermal conductivity which must be present in all real gases. Further, Welander[39] feels that the theory of the temperature-jump phenomenon is in need of modification.

The authors undertook the present investigation in an attempt to clarify at least some of the factors mentioned above. It was decided to limit the problem to a comprehensive study of accommodation coefficients on air covered surfaces. Particular attention was directed to the following: retention of the maximum possible coverage of the surface; assignment of an unambiguous temperature, within narrow limits, to the measured accommodation coefficient; proper analysis of the raw experimental results; and interpretation and evaluation of certain earlier results in the light of the present findings.

Experimental

Accommodation coefficients of H_2, D_2, He, Ne, N_2, O_2, A, Kr and Xe on unflashed tungsten, nickel and platinum wires were determined as functions of (1) pressure, at a given ambient temperature; (2) small temperature differences between the average temperature of the wire and a fixed ambient temperature, at a given pressure; and (3) ambient temperature. Apparatus design and experimental procedures were adopted which were consistent with the use of rigorous heat flow theory and kinetic theory. For example, a small temperature rise of the wire with respect to the ambient temperature is desirable to permit proper integration of the fundamental heat flow equations, to minimize changes in the condition of the wire surface, and to permit the assignment of a definite temperature, within the spread of the temperature rise, to the accommodation coefficient itself. Accordingly, temperature rises ranging from 1 to 10° were used, and a value of 2° was considered optimum. Since resistance measurements were used to determine these small rises as the difference between the ambient temperature of the accommodation coefficient cell and the average temperature of the wire, relative resistances were measured with a precision of a few parts per million in an attempt to obtain rises with an accuracy of the order of a few tenths of a per cent.

A detail of one of the arms of the accommodation coefficient is shown in Fig. 1. The wire is held coaxially in a surrounding metal cylinder by a relatively massive spring suspension which exerts a tension of 9–12 g. Both ends of the wire, electrically insulated from the surroundings, are heat stationed at the ambient temperature. The complete cell contains three such arms, one each for the tungsten, nickel and platinum wires, attached to a common manifold to assure identity of gas pressure around each wire. By using Kovar metal for the cylinder around the tungsten, and nickel for the cylinders around the other wires, it was possible to match coefficients of expansion closely enough to permit the cell to operate from 90 to 373°K. without losing tension on the wires.

To maintain the ambient temperature within required limits, the cell was immersed in an oil-bath, regulated to $\pm 0.002°$ during a set of measurements. The bath temperature was measured with a precision, platinum resistance thermometer, and a specially constructed Wheatstone bridge, both carefully calibrated. The average temperatures of the wires were obtained during a set of measurements by measuring their resistances relative to a precision standard resistance. Such resistance measurements were made potentiometrically to permit simultaneous determination of the heating current passing through the wires. The potentiometer, a Leeds and Northrup Wenner type, had been calibrated by the National Bureau of Standards and recalibrated for internal consistency before starting the present experiments. It had a range of 110,000 μv. with dials reading directly to single microvolts. The range was extended into the region of hundredths of microvolts, by galvanometer deflections whose voltage equivalents were determined at every reading. In order to give physical significance to such deflections, measurement procedures were developed which permitted adequate corrections to be made for parasitic e.m.f.'s. These e.m.f.'s, although occasionally as large as one or two μv., were constant to about 1% during the time of a set of measurements, including the readings needed for the corrections.

In order to calculate values of the accommodation coefficients, it is necessary to have numerical values of certain

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properties and dimensions of the wires. Those which were directly determined were the relative resistances as a function of temperature, the diameters and the lengths. The resistances were measured, with high pressure gas in the cell to reduce heating of the wires, as a function of current, and at several temperatures which bracketed each of the ambient temperatures at which accommodation coefficients would later be determined. Small heating effects, which could not be removed by the high pressure gas, were eliminated by extrapolating the resistances, at a given bath temperature, to zero current. The wire diameters were determined interferometrically with an accuracy which was limited by the uniformity of the wires, rather than by the method. For tungsten, nickel and platinum (nominal diameters, 4×0^{-3} cm., 5×10^{-3} cm., 5×10^{-3} cm.) the diameters are felt to be accurate to 0.8, 1.0 and 0.2%, respectively. The wire lengths, approximately 11 cm., were measured with a cathetometer during assembly of the cell arms, and are known with an accuracy of a few tenths of a per cent.

The low pressures which were required in the experiments were obtained by a series of expansions from a small known volume which contained gas at 50–200 mm. These high pressures were measured manometrically, using a cathetometer, with a precision of ±0.05 mm.

The wires (obtained from the Kulite Tungsten Co., Union City, N. J., and Sigmund Cohn, New York) were of very high purity, 99.9+, 99.9+ and 99.999+%, for the W, Ni and Pt, respectively. In the case of wires which are covered with an adsorbed layer of air, the accommodation coefficients are not sensitive to metallic impurity. However, wires of high purity have large temperature coefficients of resistance, and are therefore advantageous for accurate temperature measurement. Although the wires had been cleaned after drawing, they were repeatedly washed with pure acetone after the cell had been assembled, and then dried *in vacuo* at about 90° to remove any oil or grease films that might have remained. The cell was then re-exposed to air for several months prior to the start of measurements. Of the gases, helium and xenon were repurified before use. The helium was passed over activated charcoal at liquid nitrogen temperature, and the xenon was frozen at liquid nitrogen temperature and vacuum pumped to remove traces of air which might have been introduced during preliminary operations with the gas. The other gases were obtained in purity of 99.5% or better, and were used directly, except for passage through traps at Dry Ice or liquid nitrogen temperature enroute to the cell.

Equations

The heat conducted by a gas from an electrically heated wire, heat stationed at both ends at the temperature of a surrounding cylinder (ambient temperature), can be determined from a modified form of Verdet's differential heat flow equation.[40] This equation can be solved to give the average temperature rise of the wire, $\overline{\Delta T}$, in the form

$$\overline{\Delta T} = \frac{I^2R_0}{A\pi r_w^2K_0l}\left(1 - \frac{\tanh A^{1/2}l/2}{A^{1/2}l/2}\right)$$

where the symbols are defined as: r_w = radius of wire; I = current; R_0 = resistance of wire at ambient temperature; K_0 = thermal conductivity of wire at ambient temperature; and l = length of wire. For gases at very low pressures, the constant A is given by

$$A = \frac{2a'(C_v + R/2)P_0}{r_wK_0(2\pi RMT_0)^{1/2}}(1 - 1.1928\beta_K\overline{\Delta T}) + \frac{8\epsilon_0\sigma T_0^3}{r_wK_0}\left(1 + 1.192\overline{\Delta T}\left[\frac{1.5}{T_0} + \gamma - \beta_K\right]\right) - (\alpha - \beta_K)\frac{I^2R_0}{r_w^2K_0l} \quad (1)$$

where the additional symbols are defined as: ϵ_0 = total emissivity of wire at ambient temperature; σ = Stefan Boltzmann constant; T_0 = absolute ambient temperature; γ = temperature coefficient of emissivity; β_K = temperature coefficient of thermal conductivity of wire; α = temperature coefficient of resistance of wire; C_v = molar heat capacity of gas at constant volume; R = gas constant; P_0 = gas pressure at T_0; M = molecular weight of gas; and a' = apparent thermal accommodation coefficient. The first term in the expression for A takes into account energy conducted from the wire to the cylinder by the gas; the second term, energy radiated by the wire to the cylinder; and the third term, additional energy obtained from the increase of wire resistance with increasing temperature.

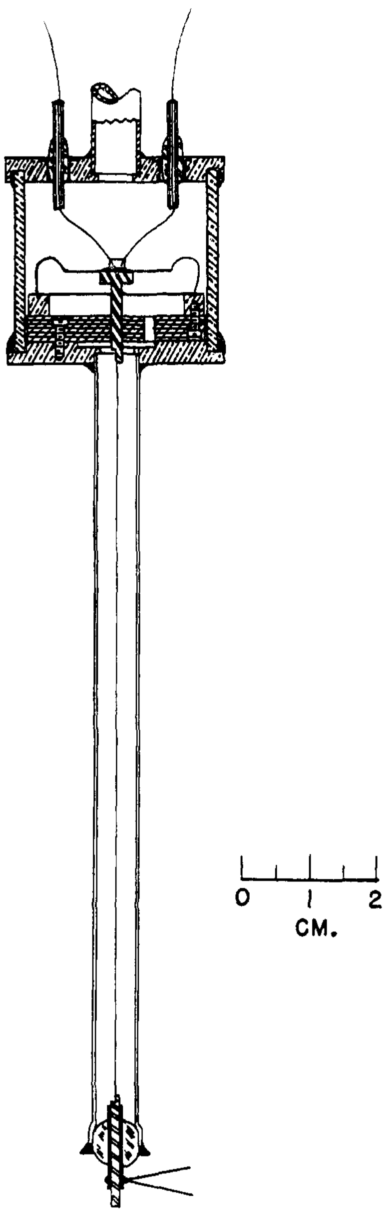

Fig. 1.—Arm of accommodation coefficient cell.

Equation 1 may be expected to yield values of the accommodation coefficient which, at a given temperature, will be independent of pressure, only

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(40) Ê. Verdet, "Théorie Mécanique de la Chaleur," mm. Prudhon et Violle, Paris, France, 1871, T II, p. 197.

TABLE 1

ACCOMMODATION COEFFICIENTS OF NINE GASES ON W, Ni AND Pt

		H_2	D_2	He	Ne	N_2	O_2	A	Kr	Xe
W	a_{25}	0.357	0.454	0.470	0.802	0.868	0.905	0.967	0.986	0.992
	$10^4\delta$	+1.2	+2.2	+1.6	−0.8	−1.9	−2.2	+2.1	+1.3	+1.0
Ni	a_{25}	0.294	0.387	0.385	0.732	0.824	0.862	0.935	0.965	0.984
	$10^4\delta$	−6.0	−3.8	−3.8	−7.0	−8.8	−6.8	−3.8	−3.2	−3.5
Pt	a_{25}	0.287	0.377	0.368	0.716	0.816	0.853	0.925	0.959	0.978
	$10^4\delta$	−6.5	−3.8	−5.0	−9.5	−9.5	−9.3	−3.8	−4.3	−4.1

at extremely low pressures where the gas conduction may be assumed to be entirely of the free-molecule type. In general, however, the apparent accommodation coefficient may be expected to decrease with increasing pressures where a significant fraction of the heat conduction is by molecular collision. For the present case of a wire of radius r_w surrounded by a cylinder of radius r_c, a relation between the true coefficient, a, and the apparent coefficient, a', was derived by assuming that (1) within a cylindrical shell of height l, and annular thickness λ, around the wire, heat is transported entirely by molecular (free-molecule) conduction. 2. Within a cylindrical shell of height l, and annular thickness λ, around the inner surface of the surrounding cylinder, heat is also transported entirely by molecular conduction. 3. In the region between the cylindrical surfaces at $r_w + \lambda$ and $r_c - \lambda$, the heat is transported entirely by molar conduction. When the usual steady-state conditions are imposed, namely, continuity of temperature from the wire to the cylinder wall, and equality of energy transport across the surfaces at $r_w + \lambda$ and $r_c - \lambda$, the above assumptions lead to the relation

$$a = a' \frac{1 + \frac{r_w}{r_c}\left[a + \frac{r_c - \lambda}{r_c}(1 - a)\right]}{1 - \frac{a' r_w (C_v + R/2) P_0}{(2\pi R M T_0)^{1/2} K_g} \ln \frac{r_c - \lambda}{r_w + \lambda}} \qquad (2)$$

Symbols in eq. 2 which have not been previously defined are λ, the mean free path of the gas at P_0, and K_g, the thermal conductivity of the gas at T_0. Equation 2 is valid for λ between 0 and $1/2(r_c - r_w)$, and predicts that the decrease of the apparent accommodation coefficient with increasing pressure should be most marked for gases of relatively small mean free paths. This prediction has been confirmed by the present results.

Results

By exercising extreme experimental precautions, particularly in connection with the electrical measurements, it was possible to limit the average temperature difference between the wire and its surrounding cylinder to two or three degrees and still obtain a precision of about one per cent. in a. Since the relative temperature coefficient of a, $(1/a)\mathrm{d}a/\mathrm{d}t$, is small, of the order of 0.001 deg.$^{-1}$, the coefficients determined in this investigation were assigned the cylinder temperature.

For each of the three wires, approximately 70 runs, each run in duplicate, were made at 9, 50 and 100° in the pressure range from 0.004 to 0.3 mm. The true accommodation coefficients calculated from eq. 2 were essentially pressure independent. The decrease in the accommodation coefficient with decreasing pressure which had been reported in several previous investigations[12,13,16] was not observed in the present case. There was, however, a small temperature dependence which could be represented within the experimental accuracy by the relation $a_t = a_{25}[1 + \delta\,(t - 25)]$. The complete results of the present investigation are summarized in Table I in terms of smoothed values of the accommodation coefficient at 25° and its temperature coefficient, δ.

On the basis of a statistical analysis of all the experimental results, the error in the tabulated values of the accommodation coefficient is estimated to be $\pm 1\%$. The uncertainty in δ is set at $\pm 1.5 \times 10^{-4}$ deg.$^{-1}$.

Discussion

The maximum average temperature rise of the wire above ambient temperature in the present determinations was rarely large enough to change the value of the accommodation coefficient as much as 1%. Temperature rises of 10° or less should not in themselves interfere with the determination of accurate coefficients. Since the temperature rises used for most of the experiments which are summarized in Table I were about 2 or 3°, the estimated error in the smoothed values is attributed to slight variations with time in the nature of the gas-covered surfaces, and to uncertainty in the values of the wire diameters. When very large temperature rises have been used, examination of the literature shows that quite reasonable concordance among the results of different investigators can be obtained if the temperature which is assigned to the accommodation coefficient is the average wire temperature, rather than the ambient temperature. This empirical observation would seem to be a natural consequence of the importance of the substrate surface in determining the magnitude of the accommodation coefficient of a given gas. In connection with this empirical rule, it must be remembered that excessively large temperature rises will probably change the extent of surface coverage, and that the qualitative character of the surface may have to be assessed in seeking concordance with other results in which different temperature rises were involved.

It is interesting to observe, in Table I, that the accommodation coefficient of the same gas is very little affected by the metal substrate. Since all wires have maximum surface coverage, the somewhat higher values on tungsten were attributed to significant surface roughness of the tungsten itself.

Electron photomicrographs at 8200 times magnification showed that the platinum surface was extremely smooth, the nickel surface just slightly rougher, while the tungsten surface showed appreciable roughness, as shown in Fig. 2. The effect of surface roughness is to increase the accommodation coefficient by permitting gas molecules to make more than one collision, on the average, before leaving the surface. For example, if a molecule makes n collisions before leaving the surface, its accommodation coefficient, a_n, in terms of the corresponding coefficient characteristic of a single collision, a, is given by $a_n = 1 - (1 - a)^n$. If the surface of platinum is assumed to be smooth enough so that its accommodation coefficients are characteristic of molecules which suffer only one collision before leaving, the value of n for tungsten varies from 1.25 at 9° to 1.40 at 100°. The corresponding value for n for nickel is close to 1.04 and substantially constant with temperature.

The most dramatic example in the literature, of the minor effect upon the accommodation coefficient of different smooth substrates which have maximum gas coverage, is found in the results of Keesom and Schmidt.[10] Their accommodation coefficients at 0° on *glass* with maximum gas coverage are in remarkably good agreement with corresponding values for Ni and Pt computed from the entries in Table I. Similarly, the results of von Ubisch[17] on unflashed tungsten and platinum also show good agreement with the results of this research. In fact, it is possible to obtain good agreement among the results of almost all investigations which have the following common characteristics: maximum coverage of the substrate with the same gas; temperature rises which permit assignment of an unambiguous temperature to the accommodation coefficient; and experimental conditions which permit correct analysis of the existing heat conduction situation. For different adsorbed gases on a given substrate, different values of the accommodation coefficient are to be expected. This is confirmed, at least qualitatively, by the results of Eggleton and Tompkins.[18] On the basis of the present results it seems very likely that the adsorbed gas layer on the W, Ni and Pt wires was essentially that which would be obtained by having exposed these wires to air at atmospheric pressure for long periods, possibly months or years, and that the extent of surface coverage was probably greater than that corresponding to true equilibrium values at the pressures in the cell.

As mentioned previously, the present investigation did not show that the accommodation coefficient decreases with decreasing pressure, although this effect had been found in other investigations. The authors are inclined to believe that both effects are possible. For example, if unflashed wires are pumped long enough and well enough, without heating, it is conceivable that part of the original adsorbed gas layer is removed, and that a partially covered surface is produced whose extent of coverage is closer to the true equilibrium value. This type of surface would be characterized by smaller accommodation coefficients. In the earlier experiments of Amdur, Jones and Pearlman on platinum,[13] the cell frequently was pumped to a stick vacuum for very long periods, often a week or more, before starting the lowest pressure runs, and the lower accommodation coefficients were observed at these pressures. In the present investigation, on the other hand, where pumping times were considerably shorter, and precautions were taken to keep the nature of the unflashed surfaces as intact as possible, no pressure dependence was observed. It would seem desirable to have further systematic investigation of the effect of vacuum treatment upon the accommodation coefficients obtained with unflashed wires.

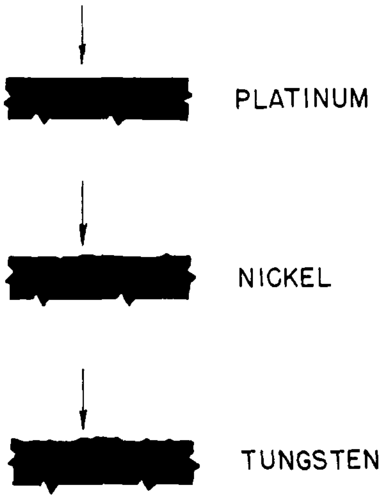

Fig. 2.—Tracings of electron photomicrographs. Arrows indicate wire surfaces.

The small, negative temperature coefficients of the accommodation coefficients on nickel and platinum is attributed to a slight decrease, with increasing temperature, of the fraction of surface covered by adsorbed gas. This explanation is consistent with the observation that the coefficients on bare wires are frequently as small as 10% of those on unflashed wires. In this connection, it is interesting to observe that tungsten, whose value of δ, within the experimental uncertainty, is virtually zero, is known to exhibit extremely strong adsorption at ordinary temperatures.[41,42]

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