

Thermal Accommodation Coefficient of Gases on Controlled Solid Surfaces: Argon–Tungsten System

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The knowledge of the thermal accommodation coefficient for gases on well-controlled surfaces as a function of temperature is imperative to understanding the mechanism of interphase heat transfer on the microscopic level. With this goal in view, a heat transfer column instrument is designed, fabricated, assembled, and tested for the specific case a argon–tungsten system. With 99.9999%, pure argon, six sets of data are taken in the rarefied gas region in the maximum temperature range of 500–1500 K. Four sets of these measurements are in the temperature-jump region and are analyzed by the constant-power method to compute the thermal accommodation coefficient of argon on a controlled tungsten surface. The other two sets are taken under free-molecular flow conditions and are interpreted in accordance with the man-free-path kinetic theory for the low-pressure regime. These data are compared and discussed in the context of reported data in the literature and interpreted in the light of the surface condition and finish of the tungsten wire.

KEY WORDS: argon gas; thermal accomodation coefficient; tungsten surface.

1. INTRODUCTION

The measure of efficiency with which a gas exchanges heat with a solid surface is known as the thermal accommodation coefficient, α . It is usually expressed in terms of the temperatures of the incident molecules, T_i , the reflected molecules, T_r , and the surface temperature, T_s , such that²

$$\alpha = (T_r - T_i)/(T_s - T_i) \quad (1)$$

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² For an explanation of symbols, see Nomenclature.

This definition, however, is not very appropriate and has been criticized [1]. It is pointed out that the collision process in a gas stream–solid surface system cannot in general be expressed by associated temperatures for the simple reason that the reflected molecules may well have a non-equilibrium distribution to which no temperature is assignable. Hence, it is meaningful to interpret the extent of accommodation in terms of the energies of various gas streams. In other words, α is the ratio of the actual heat transfer rate, Q_H , to its value Q_{KT} , which would have been obtained if the impinging gas molecules came to complete thermal equilibrium with the solid surface, that is,

$$\alpha = Q_H/Q_{KT} \quad (2)$$

The quantity Q_H represents the net difference of the total reflected energy flux, E_r , and the total incident energy flux, E_i , whereas Q_{KT} accounts for the net difference of the total reflected energy flux obtained on the assumption that the interaction between the gas and the solid atom is complete, E_s , and the total energy flux. The former, $(E_r - E_i)$, is experimentally measurable, while the latter, $(E_s - E_i)$, must be obtained by the application of kinetic theory.

The surface condition plays a dominant role in the measurement of thermal accommodation coefficient for any gas–solid system. As a matter of fact, the interpretation of the α value is inseparable from the specification of the surface state on the molecular level [2]. A general status of the knowledge of gas adsorption on solid surfaces is reported by Saxena and Joshi [1] and relevant information is given later in this work. Here we report the thermal accommodation coefficient for an argon–tungsten system as determined from heat transfer rate data taken in the temperature-jump and free-molecular flow regimes. The constant-power and mean-free-path kinetic theory methods developed for the two regimes, respectively, are employed to compute α from heat transfer data. The experimental work is performed on a specially designed heat transfer column instrument so that the heat transfer surfaces are not contaminated with hard-to-remove adsorbed gases. The α values are critically analyzed in the light of the surface condition and purity. The preparation and maintenance of an atomically uniform and clean surface are essential in the measurement of the thermal accommodation coefficient of a gas on a solid surface and have been achieved in the present work.

In recent years, we [3–12] have measured α for a number of gas–solid systems as a function of temperatures, and these are listed in Table I. In these measurements, the exact specification of the surface condition of the wire has not been possible and the surfaces are generally referred to as gas-

Table I. Summary of Gas-Solid Systems for Which α Has Been Measured by Saxena et al.

Investigators	Gas-solid system	Temperature range (K)	Pressure range (Torr) ^a	Reference No.
Chen & Saxena	Nitrogen-tungsten	450-1450	8.0-100	3
Jody & Saxena	Neon-tungsten	300-2600	6.0-150	4
Chen & Saxena	Argon-tungsten	600-2500	5.0-7	5
Chen & Saxena	Argon-tungsten	550-2500	5.0-60	6
Jode et al.	Neon-platinum	400-1400	6.1-15	7
Jody et al.	Krypton-platinum	400-1400	0.5-10	7
Saxena & Chen	Nitrogen-tungsten	500-2500	4.7-50	8
Saxena & Chen	Carbon dioxide-tungsten	500-2000	3.8-55	8
Jody & Saxena	Helium-tungsten	700-2300	16.1-89	9
Jody et al.	Helium-tungsten	300-1400	54.0-95	10
Afshar et al.	Sulfur dioxide-platinum	630-1210	5.0-31	11
Afshar et al.	Argon-platinum	400-1350	5.0-21	12

^a One Torr (1 mm Hg) is equal to 133.3 Pa.

covered engineering surfaces. The platinum wire used is about 99.96% pure and the metallic impurities from bulk platinum will diffuse to the surface under extensive heating while annealing at temperatures above 1000 K. The rate of diffusion is rather slow below 1000 K [13]. Additional contamination of the platinum surface will result from the adsorption and reaction of gases other than the test gas. It is shown by Jody and Saxena [9] that, in a column instrument, there can be an appreciable contribution by the desorbing oxygen from surfaces other than the test surface. As no special care was taken to desorb the column surfaces, we would expect some oxygen contamination. As mercury was also present in the system, it is likely that gas adsorption on platinum might have been poisoned, a property observed by Chapman and Reynolds [14]. Once the surface is contaminated, it is not possible to clean it thermally at about 1273 K [15]. The interaction of oxygen with platinum is very complicated because, in addition to simple adsorption, it can oxidize the platinum as well as the metallic impurities present in the sample.

The adsorption of oxygen in its different forms on tungsten gives rise to one of the most stubborn layers to remove. Wachman [16] concluded that three and possibly four types of oxygen films form on the tungsten surface and that the adsorption of oxygen is irreversible with pressure. In other words, it does not get desorbed by lowering the level of pressure at a

constant temperature. In addition, the adsorption of oxygen on tungsten takes place over a wide temperature range. Gomer and Hulm [17] found that at temperatures as low as 20 K, oxygen gets chemisorbed on tungsten, whereas the physically adsorbed oxygen on tungsten is negligible. Geus [18] observed that at temperatures above 195 K, the initial rapid chemisorption process is followed by a slow uptake of more oxygen. Ptushinskii and Chuikov [19] reported additional adsorption of oxygen above 900 K. van Cleave [20] found an increase in the α of a Ne-W system in the temperature range 1500–1700 K, which he attributed to further adsorption of atomic oxygen due to the rearrangement of the oxygen atoms in the adlayer in this temperature range.

Further, while oxygen can be adsorbed on all the sites in tungsten [21] forming a complete monolayer, nitrogen covers only a portion of a monolayer when it is in the pure state [19]. Oxygen also replaces some of the nitrogen adsorbed on the tungsten and drastically reduces the adsorption of carbon monoxide [22]. The adsorption of hydrogen and monatomic gases such as neon and argon is negligible. Thus, it is apparent that adsorbed oxygen is the dominant species on the tungsten surface. The effect of pressure changes on the adsorption of gases on tungsten including oxygen has been investigated by Morrison and Roberts [23]. They observed a change in α for the Ne-W system at about 300 K from 0.057 for a bare surface to 0.226 for the same system after the surface was exposed to oxygen at a pressure of less than 10^{-7} Torr (1.333×10^{-5} Pa). When the pressure was increased to about 4×10^{-7} Torr (5.332×10^{-5} Pa), the value of α increased less rapidly to 0.27. After heating the tungsten wire to about 1100 K, the value of the coefficient dropped to 0.177, and further heating had no effect on α until the temperature of the tungsten wire exceeded 1700 K. According to them, the stable layer which stayed undisturbed up to about 1700 K was made up of atomic oxygen. Thus, it is clear that the preparation and characterization of a controlled surface are extremely difficult, and in the following we describe a column instrument designed to accomplish this goal for the measurement of α for gas-solid systems.

2. EXPERIMENTAL

The column instrument whose schematic is shown in Fig. 1 is designed primarily to cope with some of the difficulties arising in the measurement of heat transfer in temperature-jump and free-molecular flow regimes. As will be seen, attempts are made here to maintain a uniform and controlled solid surface in order to understand clearly the effects of adsorption, to be able to quantify the amount of gas adsorbates, and to reduce the partial pressure of impurities introduced, by different means, into the gas phase.

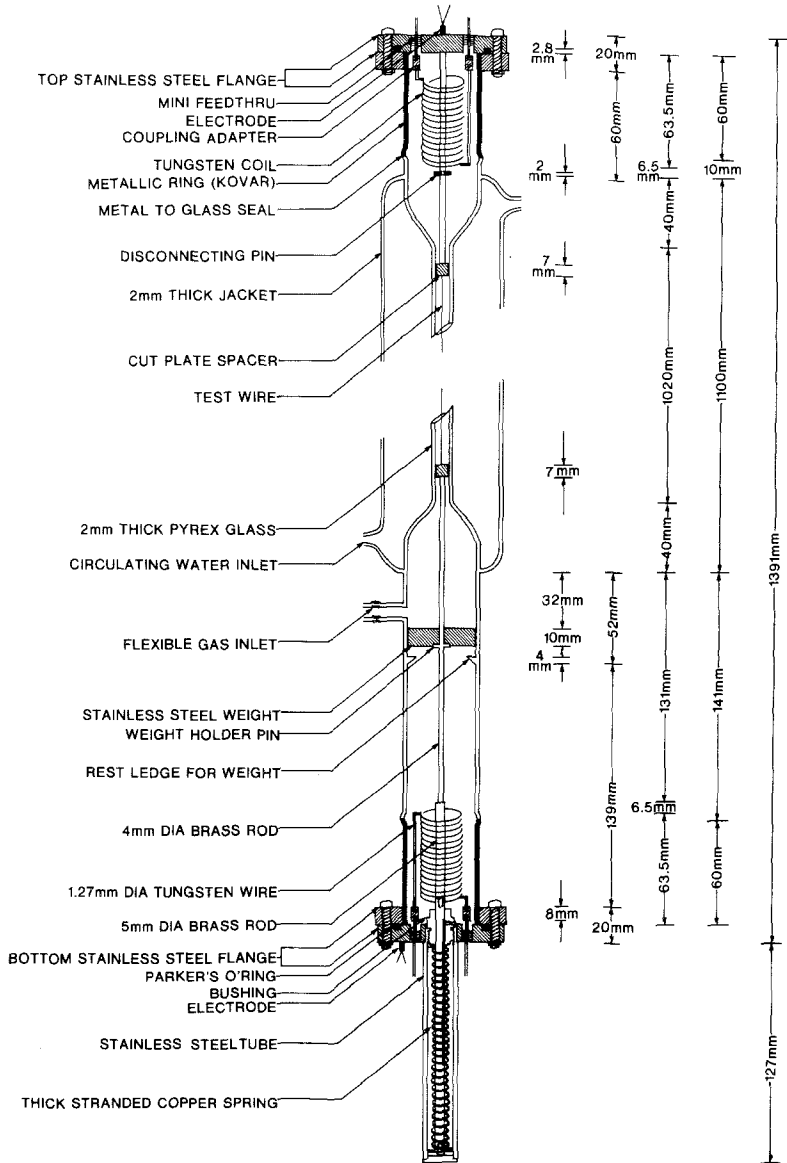


Fig. 1. A schematic of the heat transfer column instrument for the measurement of the thermal accommodation coefficient as a function of temperature for gases on controlled solid surfaces.

Broadly speaking, the column may be viewed as consisting of four sections. The central test section is comprised of a jacketed 8-mm Pyrex glass tube (2-mm wall thickness) about 100 cm long. The outer diameter of the 2-mm-thick glass jacket is 70 mm. The two bottle-shaped top and bottom compartments are similar in most of their structural details. The bottom compartment is longer than the top compartment and it houses a stainless-steel weight to provide proper tension to the test wire, which hangs taut axially in the central test section. Both of these top and bottom glass compartments are provided with glass to kovar seals and are vacuum sealed by metal flange joints. The inner plate of the flange joint whose details are shown in Fig. 2 is heliarck welded to the kovar ring. The outer plate whose design details are given in Fig. 3 is bolted to the inner plate by six equally spaced bolts with a Parker's O'ring sandwiched between them. To the outer plate of the bottom flange is welded a stainless tube 20 mm in outer diameter and 127 mm in length referred to here as the lower end section. It houses a thick-stranded copper spring attached to a 5-mm-diameter brass rod. The latter passes through a bushing whose details are given in Fig. 4. The expansion of the wire as it is heated to different temperatures is absorbed by a thick-stranded copper spring in the lower end section.

The test wire in the central section is held axially with the help of two cut-plate spacers of the design shown in Fig. 5. The design of the stainless-steel weight is sketched in Fig. 6, and its function is to provide adequate

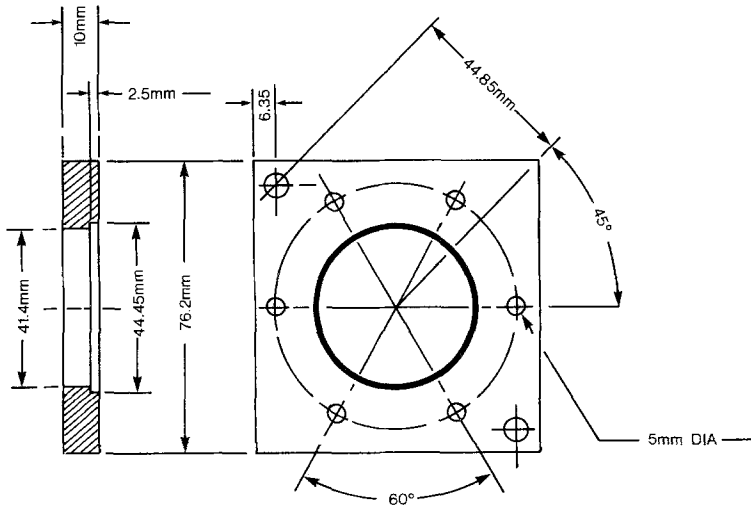


Fig. 2. The details of the inner plate heliarck welded to the column at the top and bottom flange joints

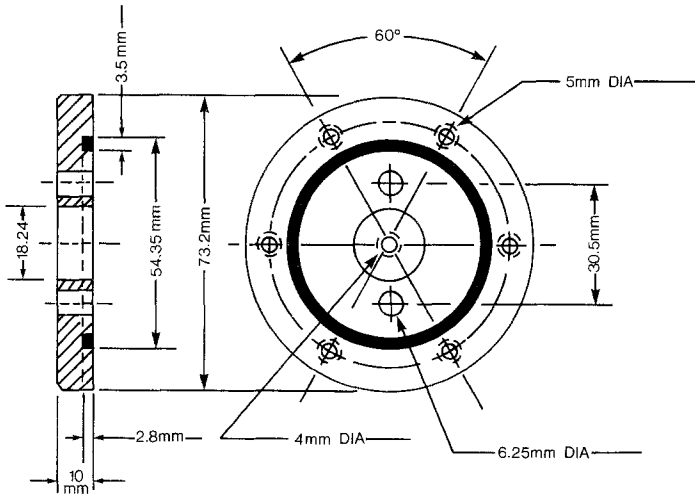


Fig. 3. The details of the outer plate attached to the column at the top and bottom flange joints.

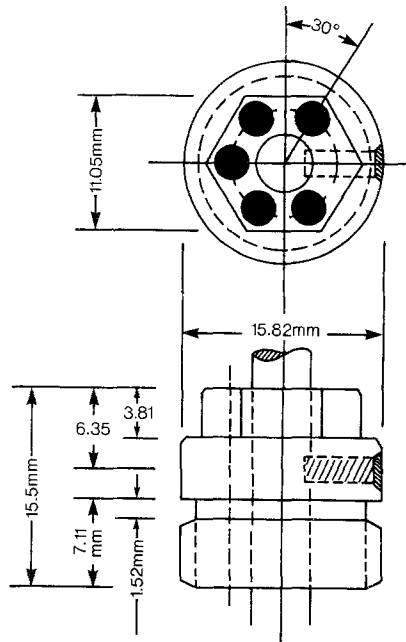


Fig. 4. The horizontal and vertical cross sections of the bushing.

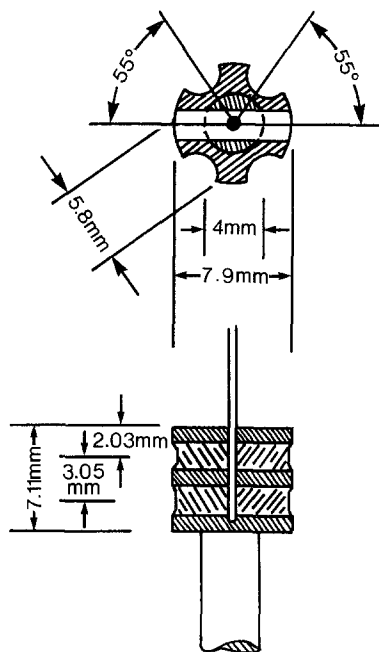


Fig. 5. The horizontal and vertical cross sections of the cut-plate spacer.

pull to the wire so that it remains taut and hence axial in the vertical central section. The top and bottom compartments are also each equipped with a 12-mil heating tungsten-wire coil with a winding diameter of 24 mm which is secured in position by the support of two 50-mil tungsten rods. These rods are connected to two electrical mini-feed-thrus welded to the outer plate flange unit through two small adaptors. The feed-thrus, supplied by Cermaseal Inc., New York, have the rating of 100 V and 15 amp. The conductors of feed-thrus are made of 50-mil-diameter copper wire and are energized by an AC source via a variable-voltage transformer.

The two tungsten coils in the top and bottom compartments also serve the purpose of being getters and effective traps for the possible impurities in the test gas and the desorbing molecules either from the filament or from the glass surface. It may be pointed out that the choice of the tungsten wire as the coil material is due to its high melting point, its high tensile strength at high temperatures, and the ease with which it can be cleaned for adsorbed gases. The minor thermal expansion of the kovar rings due to heating will move the column up in view of its rigid mounting at the bottom end on a metal frame and will be absorbed by the flexible gas inlet connection.

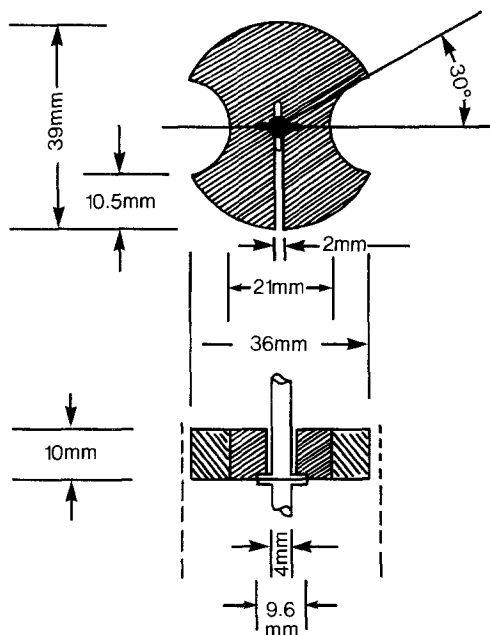


Fig. 6. The horizontal and vertical cross sections of the stainless-steel weight loaded on the axial rod.

The test tungsten-wire surface will get contaminated rapidly as its temperature is lowered by the adsorption of desorbing molecules from the cold surface of the column [1]. It is therefore imperative that all possible sources of contaminants must be properly treated to keep the desorption from column walls at negligible level. The above-mentioned tungsten coils are one such device. Another is to gold coat the test section and further gold electroplate all the metallic surfaces, other than the test tungsten wire and the two tungsten coils. The gold coating on the glass wall is done by painting the surface with an organic gold compound which is then baked at a temperature slightly above the evaporation temperature of organic material. The glass surface is then left with a thin layer of pure gold.

It is known [24] that gold does not adsorb most gases including oxygen, which is a dominant adsorbate in the column. However, oxygen is chemisorbed on the gold surface. The oxide formation becomes somewhat rapid above 500°C at pressures of about 10^{-6} mm Hg and the resulting gold oxide will remain strongly bound to the surface. If the pressure is as low as 10^{-8} mm Hg, the rate of chemisorption is reduced.

The axial wire serves both as a heater and as its own resistance ther-

mometer. For the latter purpose, a well-annealed sample of tungsten wire is calibrated by the measurement of its resistivity at the triple point of water and at the freezing points of tin, cadmium, zinc, and aluminum [25]. The following polynomial in temperature, $T(\text{K})$, represents the resistivity, $\rho(\mu\Omega \cdot \text{cm})$, and is used to establish the temperature of the wire from its resistance measurement:

$$\rho(T) = \sum_{j=0}^4 C_j T^j \quad (3)$$

Here, $C_0 = -0.202 \times 10^{-6}$, $C_1 = 2.000 \times 10^{-8}$, $C_2 = 1.549 \times 10^{-12}$, $C_3 = 4.321 \times 10^{-15}$, and $C_4 = 1.208 \times 10^{-18}$. The tungsten wires are annealed under vacuum in a separate column in order to prevent the contamination of this specially designed column by elements such as carbon and different kinds of oxides. The process of annealing the tungsten wire necessitates a gradual heating in steps to the highest temperature of about 2500 K and maintaining it at that temperature for a period of 2 to 3 h.

The loading of the wire is done simply by raising the top outer flange plate and lowering the lower end section with the help of the thick-stranded copper spring housed in the lower section. The outer flange plates are then bolted to the inner plates and then the gold-plated stainless-steel weight is loaded to the wire with the help of a strong magnet. This provides proper tension to the wire and thus keeps it straight and central in the glass tube. The system is then tightly closed and pumped down to a residual pressure of 10^{-10} mm Hg (1.333×10^{-8} Pa). For the purpose of cleaning, the test wire and the two tungsten coils are heated up to a temperature of about 2500 K, while the system is still open to the pumps. After a period of 2 to 3 h the tungsten coils are allowed to cool down in steps, while the test wire is still maintained at the highest temperature. This will enable the last oxygen molecules flowing in the column to adsorb preferentially on the cold tungsten coils. Before introducing a gas for measurement, it is preferable to wash the system with the same test gas to ensure that all impurities are diluted and pumped out. The test wire is then cooled down slowly and the system is isolated from the pumps. Since this system is built for temperature-jump and low-pressure regimes, the pressure measurements are made on absolute and McLeod gauges, respectively.

With argon gas of 99.9999% purity we have taken six sets of data, in the maximum temperature range of 500 to 1500 K, under the gas rarefied conditions. Four sets of these measurements are in the temperature-jump region and are analyzed by the constant-power method in order to compute the thermal accommodation coefficient of argon on a controlled tungsten surface. The other two sets are measured under free-molecular

flow condition and are interpreted in accordance with the mean-free-path kinetic theory for the low-pressure regime. The column is fitted with a 56-cm-long tungsten wire having a diameter of 0.3054 mm. The tungsten wire is annealed for 6 h at a temperature of 2500 K, then for 2 h at a temperature of 1500 K, and thereafter for about 5 min at a temperature of 1500 K before each set of measurements. The temperature of the outer wall of the column is maintained at 316 K and is kept constant throughout the experiment. Experimental data are taken in the pressure range of 1.1 to 3.0 cm Hg (1.4663–3.999 kPa) and, for the entire temperature range, conform to the requirement of the theory of heat transfer for the temperature-jump regime. The pressures are measured by an absolute gauge with a range of 0 to 10 cm Hg (0–13.33 kPa). For the free-molecular flow region, the heat transfer rate data are measured at pressures of 0.012 and 0.10 mm Hg (1.5997 and 13.33 Pa) as measured on the McLeod gauge. In the analysis of heat transfer in the continuum regime, it is shown [26] that the thermal energy transported by convection and end effects is negligibly small compared to the total heat transfer. Under rarefied conditions, the contributions of convection and end effects are still smaller, and consequently the heat transfer in the column takes place predominantly via radiation and conduction only. The conductive terms are then utilized to compute α according to a procedure which is outlined in the next section.

3. RESULTS AND DISCUSSION

If the gas mean free path is not sufficiently greater than the characteristic dimension of the hot surface, then a temperature discontinuity at the metal–gas interface develops. As the temperature increases, the pressure characterizing the onset of heat transfer by the conduction mode increases and, as a result, the temperature-jump regime extends over a large pressure range. This is explained by the fact that the mean free path of the gas at a fixed pressure increases with temperature. If the linearly extrapolated temperature of the bulk gas at the hot-wire surface is T_e , then

$$T_H - T_e = -g(\partial T/\partial r)_{r=r_f} \quad (4)$$

where g is the temperature-jump distance. Figure 7 displays a schematic representation of the temperature profile near the hot-wire surface [27]. Under well-defined approximations, Harris [28] has derived the following relation on the basis of the man-free-path kinetic theory:

$$T_H = T_e + \left[\frac{Q_H}{4\pi L r_f} \left(\frac{\pi M T_e}{2R} \right)^{1/2} \left(\frac{2 - \alpha}{2\alpha} \right) \right] \frac{1}{P} \quad (5)$$

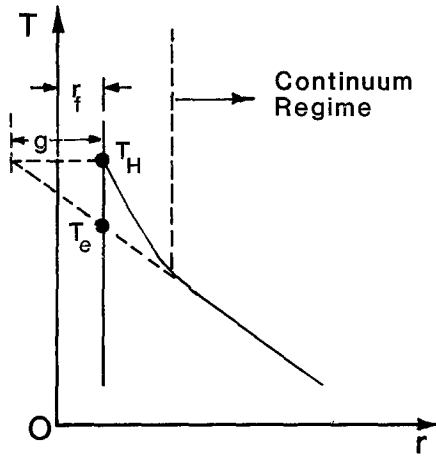


Fig. 7. Schematic representation of the gas temperature distribution near the hot-wire surface [27].

Here it is assumed that the gas pressure is high enough so that the terms involving second and higher powers of $(1/P)$ are negligible compared to the terms containing $(1/P)$. The constant-power method of determining α is based on Eq. (5). If Q_H is held constant for a given wire, the temperature distribution in the bulk of the gas, and hence T_e , will be independent of the gas pressure. Consequently, a plot of T_H versus $(1/P)$ for a constant value of Q_H will be linear with T_e as the intercept. Hence a combined knowledge of the intercept and slope will enable the determination of α as a function of T_e .

The above-mentioned constant-power method is employed in Fig. 8 to determine α . T_H is plotted versus $1/P$ for constant values of $(Q_H/2L)$. These data uphold the prediction of theory expressed by Eq. (5), to the extent that these plots are linear with T_e as the intercept. The slopes of these linear plots have been used to determine α as a function of T_e , and these are reported in Table II and are plotted in Fig. 9.

The energy of a gas stream containing N monatomic molecules and striking a solid surface of area A is [1, 29]

$$E_g = AP(2R/\pi MT_g)^{1/2} T_g \quad (6)$$

The reflected gas stream, after having achieved thermal equilibrium with the facial atomic layer of solid, will possess the following energy:

$$E_s = AP(2R/\pi MT_g)^{1/2} T_g \quad (7)$$

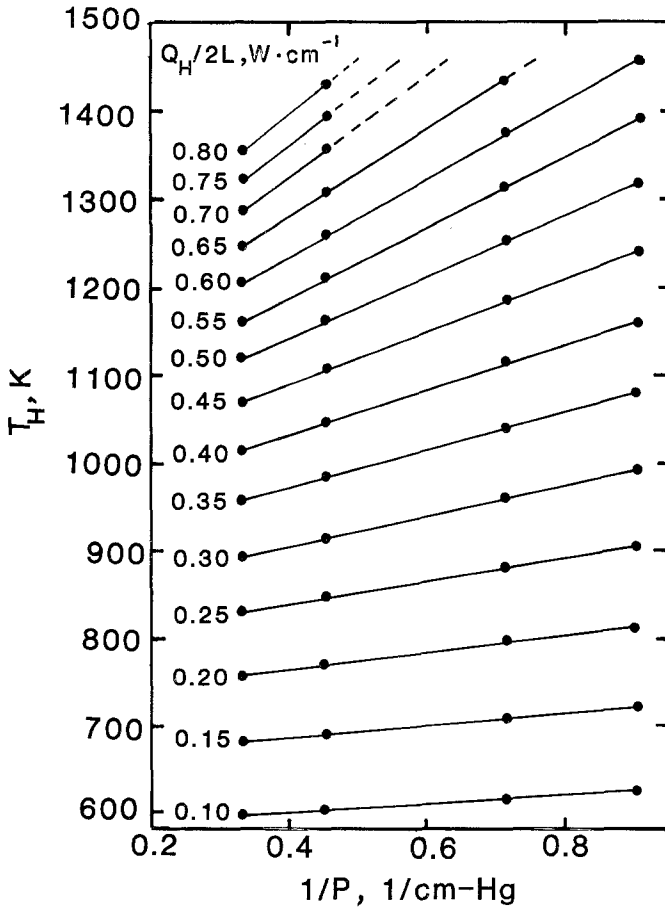


Fig. 8. Dependence of the hot-wire temperature on the argon gas pressure when constant power is fed to the wire.

Hence

$$Q_{KT} = AP(2R/\pi MT_g)^{1/2}(T_H - T_g) \tag{8}$$

and

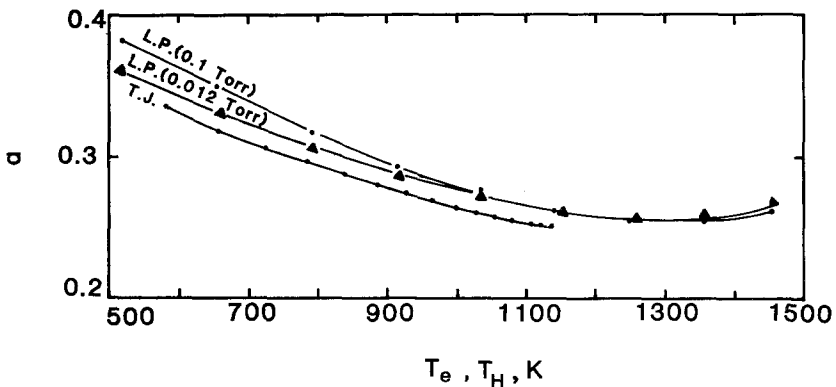
$$\alpha = Q_H/AP(2R/\pi MT_g)^{1/2}(T_H - T_g) \tag{9}$$

The α values obtained from the heat transfer data taken in the free-molecular flow regime and analyzed in accordance with the low-pressure method, Eq. (9), are also listed in Table II and plotted in Fig. 9.

Table II. Thermal Accommodation Coefficients for Argon–Tungsten in the Temperature-Jump (TJ) and Low-Pressure (LP) Regions

TJ regime		LP region		
T_e	α	T_H	α	
	11–33 Torr		0.1 Torr	0.12 Torr
584	0.337	512	0.382	0.358
657	0.320	656	0.350	0.333
722	0.307	790	0.319	0.308
836	0.288	916	0.295	0.290
928	0.276	1034	0.274	0.272
1000	0.265	1146	0.262	0.263
1056	0.259	1253	0.255	0.255
1108	0.254	1356	0.255	0.257
1136	0.250	1456	0.262	0.266

It should be noted that the adsorbed oxygen at room temperature seems to be made of two films; one is stable up to about 1000 K, and the other up to about 1800 K. The presence of these gas films has been substantiated by Wachman [16]. Morison and Roberts [23], as mentioned earlier, concluded that the stable layer which stays undisturbed up to about 1700 K is made up of atomic oxygen. The dissociation of oxygen molecules to atomic oxygen is attributed to the destruction of the chemical bonds holding the molecule together by the surface forces of the adsorbent [30].

**Fig. 9.** Thermal accommodation coefficient (α) as a function of temperature (T_e , T_H) for the argon–tungsten system.

Ageev and Inov [30] hypothesized that the molecule is first physically adsorbed, then dissociates and chemisorbs on the solid surface.

The tungsten wire used in these experiments for the determination of α values of argon on tungsten surface was fully saturated with air components at room temperature. For 2 h of heating at a temperature of about 1500 K after annealing and under a pressure of 10^{-4} mm Hg (1.333×10^{-2} Pa), most of the adsorbates will desorb from the crystalline sites. According to the observations quoted in the above discussion, only a layer of atomic oxygen will remain adsorbed on the surface. The desorbed gas molecules will not be able to reside on the metal mounting parts or on the outer wall of the test tube for they are gold plated and gold coated, respectively. It should be noted that even in the case of formation of the gold oxide, it remains strongly bound to the surface and will not be a source of contamination. The two tungsten coils mounted at the top and bottom compartments are gas saturated and will hardly be receptive to the adsorption of desorbing molecules from the wire as it is heated. The sticking coefficients for these coils can be estimated to be very low, of the order of zero [1, 31]. Further, the system is supplied with Teflon stopcocks to prevent silicone grease contamination. Chang [32] reports that the main contaminants on unannealed silicon samples that are chemically etched are oxygen and carbon. With all these possible sources of contaminants under control, the desorbing molecules will either have to reside on the glass walls far away from the test area or have to be removed to a residual pressure of about 10^{-4} mm Hg (1.333×10^{-2} Pa). Limited by this pressure residue and the impurity pressure of the test gas (100 ppm), we have succeeded in producing a solid surface covered with a monolayer of atomic oxygen. We refer to the estimation of the surface coverage later. The problem of the gas impurities and the desorbing gas molecules in the annulus can easily be solved by activating the two tungsten coils as getters and modifying the vacuum system so that a low pressure of 10^{-10} Torr (1.333×10^{-8} Pa) or lower is attainable. However, as soon as the hot wire is cooled down to the room temperature, it will adsorb some of the gaseous molecules present in the annulus. A number of available molecules of adsorbates may end up in the gaseous phase as contaminants to the test gas.

One way to characterize the tungsten surface qualitatively is to utilize the α values obtained here for the argon–tungsten system in conjunction with the thermal accommodation coefficients of argon on clean tungsten and with the information available on the adsorption of gases on a tungsten crystalline surface. However, contrary to the case of helium–tungsten, there are not sufficient data available for the thermal accommodation coefficient of argon on tungsten, especially at high temperatures.

Roach and Thomas [33] have carried out the measurement of α in the temperature-jump region for the maximum temperature range of 135 to 795 K. They have interpreted the data by both the constant-temperature difference method and the constant-power procedure. The agreement between the two sets of values is, in general, reasonable. The gas purity is specified as "highly purified grade" and the solid surface is characterized as "surface finish." Their data (curves 4 and 5) for the temperature region of 500–800 K, with the present work (curve 1), are displayed in Fig. 10. Their low values of α can be attributed to the extra clean nature of their test surface. One factor could also be the smoothness of the surface as a result of the limited time allowed for annealing. Another set of measurements in the temperature-jump region for the extended temperature range 500–2500 K is undertaken by Chen and Saxena [6]. Their surface was gas saturated, and as expected their α values (curve 8 in Fig. 10) are higher than the present data by about 30%. The temperature dependence of α shows a minimum at

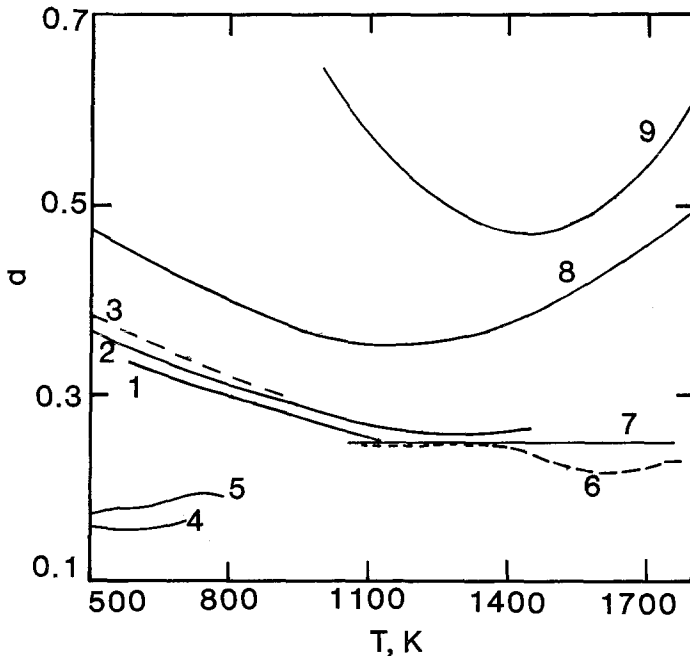


Fig. 10. Thermal accommodation coefficient as reported by different workers as a function of temperature. Curves 1, 2, and 3—present work; curves 4 and 5—Roach and Thomas [33]; curve 6—Watt et al. [36]; curve 7—Watt and Moreton [35]; curve 8—Chen and Saxena [6]; curve 9—Lim [4].

about 1100 K, indicative of the consistent desorption up to this temperature and the process of increasing adsorption at temperatures beyond 1100 K as explained by Jody and Saxena [9]. In Chen and Saxena's work, the data are interpreted by both the constant-temperature difference method and the constant-power procedure. The constant-power method yields α values consistently lower by a few percent than those obtained by the other method.

There are also three sets of data taken in the free-molecular flow regime at high temperatures, above 1000 K. The values of α measured by Lim [34] in the temperature range 999–2674 K and in the pressure range of 1.2×10^{-4} to 1.2×10^{-2} mm Hg (curve 9) are displayed in Fig. 10. The tungsten surface is conditioned by heating it at about 2700 K and at 7.6×10^{-6} Torr (1.013×10^{-3} Pa) of oxygen pressure for at least 48 h. The high α values obtained in this case may be explained in terms of the surface roughness. Around the temperature of 1000 K, the α values are about 60 to 80% higher than the values obtained by Chen and Saxena [6] for the gas-saturated surface.

Two sets of thermal accommodation coefficients in the temperature range of 1073 to 1785 K for argon on a clean tungsten surface are also found in the literature. The first set is measured in the pressure range of 1×10^{-3} to 6×10^{-3} Torr (0.1333–0.7998 Pa) by Watt and Moreton [35]. The α values so obtained do not show any dependence on pressure or on temperature. The second set is measured at 2×10^{-7} mm Hg (2.666×10^{-5} Pa) by Watt et al. [36] and exhibits only a slight dependence on temperature. These two surfaces have been electrolytically polished and the clean lines of the second surface are examined by X-ray diffraction and optical microscopy. These two sets of data (curves 6 and 7) are plotted in Fig. 10. The present data taken in the low-pressure regime (curves 1 and 2) shown in Fig. 9 and listed in Table II are analyzed here in reference to these results [35, 36]. As pointed out, besides the cleanliness of these two surfaces, the impurities in the gaseous phase are specified to be oxygen (0.8 ppm) and nitrogen (6.6 ppm). In the region of overlap the α values of the present work are higher than the data of Watt et al. [35, 36] by less than 10%. This is considered reasonable because the surface utilized in our present work is covered with a monolayer of atomic oxygen. The maximum possible coverage of the tungsten wire on the basis of impurities in the gaseous phase is less than 1%. This is elaborated on further.

We develop here a semiquantitative analysis in order to estimate the amount of coverage and the sticking coefficient. Oxygen can be adsorbed on all the crystalline sites in tungsten [37], forming a monolayer, whereas nitrogen covers only about 50% of a monolayer when in the pure state. Further, because of its affinity for tungsten, oxygen replaces some of the

nitrogen adsorbates and prevents the adsorption of carbon monoxide on tungsten. The adsorption of hydrogen, neon, and argon is negligible. This assumption will reduce the complexity of investigating a monolayer with more than one adsorbate. The system is under a residual pressure of 1×10^{-4} torr, and the impurity pressure of the argon test gas is also 1×10^{-4} Torr. Assuming an ideal gas situation in the room temperature, the total number of gas molecules present in the annulus is 6.28×10^3 . Further, the number of adsorption sites per square centimeter of the geometrical surface area for tungsten [38] is given to be 10^{15} . Thus, for a surface area of 5.36 cm^2 , the total number of available adsorption sites is 5.36×10^5 , which covers only 0.58% of the total surface area of the wire, as pointed out previously.

As mentioned earlier, one of the parameters one tries to determine in the study of adsorption phenomenon is the sticking coefficient. According to Langmuir [38], the adsorption of diatomic molecules involving their dissociation into atoms requires two adjacent adsorption centers so that

$$s/s_0 = (1 - \theta)^2 \quad (10)$$

where s_0 is the initial sticking coefficient. In our case, the coverage of the tungsten surface is such that θ is almost unity, so that s will approach zero. This is supported by the observation made by Singleton [37] in his experimentation measuring the oxygen coverage on a tungsten surface. According to him, after the surface coverage ratio (θ/θ_{300}) approaches unity for the surface flashed at 2570 K, the sticking coefficient decreases to about 10^{-3} of its original value at 300 K; θ_{300} is the coverage at the temperature of 300 K. This indicates that the probability of adsorption on tungsten crystalline sites is very small when the surface is fully covered with atomic oxygen.

The present data further indicate that as the pressure increases, the thermal accommodation coefficient increases. The trend continues up to a temperature of about 1000 K. We consider this effect to be due to the amount of coverage of atomic oxygen adsorbates, the details of which are as follows. For the temperature-jump region, the heat transfer measurements were taken after the annealed wire was heated for 2 h at 1500 K under a tight vacuum of 1×10^{-4} Torr and thereafter for 5 min before each set of measurements. This ensured the existence of a monolayer coverage of the wire for the entire period of the experimentation. An atmospheric air pressure was then introduced into the column and evacuated again. Consequently, the test surface was conditioned to a multilayer coverage as described earlier. The wire was heated again for 5 min at a temperature of 1500 K to let all the multilayer adsorbates be desorbed

from the surface of the first layer coverage. However, this may not have been enough to remove the second layer completely. The partial remains of this layer will ultimately desorb into the gaseous environment when the heat transfer measurements are taken for argon gas of 0.1-Torr pressure in the temperature range 500–1000 K. The measurements in the temperature range 1000–1500 K for the same pressure and for the entire temperature range of 0.012-Torr argon gas pressure are taken in the presence of an atomic oxygen monolayer according to the discussion presented earlier. The characterization of the two surfaces clearly explains the pressure dependence of the thermal accommodation coefficient in the temperature range of up to about 1000 K and substantiates the observations made earlier by other workers [16, 37, 23] regarding the formation of doubly absorbed gas films on a tungsten surface at room temperature.

NOMENCLATURE

A	area of the solid surface
C_j	constants in Eq. (3); $j=0, 1, 2, 3,$ and 4
E_i	incident energy flux
E_r	reflected energy flux
E_s	reflected energy flux when the interaction between the gas and the solid atoms is complete
g	temperature-jump distance
L	half-length of the metal wire
M	molecular weight of the gas
P	gas pressure
Q_H	total thermal energy conducted by the gas per unit time from the hot surface
Q_{KT}	total thermal energy conducted by the gas per unit time if the striking gas molecules were to attain thermal equilibrium with the hot surface
R	molar gas constant
r	radial coordinate
r_f	radius of the hot wire
S	sticking coefficient
S_o	initial sticking coefficient
T	temperature
T_c	linearly extrapolated gas temperature on the hot-wire surface
T_g	temperature of the impinging gas molecules
T_H	temperature of the hot surface
T_i	temperature of the incident gas stream

T_r	temperature of the gas molecules receding after collision with the solid surface
T_s	temperature of the solid surface

Greek Symbols

α	thermal accommodation coefficient for the gas–solid surface
ρ	resistivity of the metal wire
θ	gas coverage on the solid surface

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