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THE THERMAL ACCOMMODATION COEFFICIENT:
A CRITICAL SURVEY

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HAROLD Y. WACHMAN

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SPACE SCIENCES LABORATORY

GENERAL  ELECTRIC

MISSILE AND SPACE VEHICLE DEPARTMENT

SPACE SCIENCES LABORATORY

ADVANCED AERODYNAMICS OPERATION

THE THERMAL ACCOMMODATION COEFFICIENT:
A CRITICAL SURVEY*

by

H. Y. Wachman

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MISSILE AND SPACE VEHICLE DEPARTMENT

GENERAL  ELECTRIC

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THE THERMAL ACCOMMODATION COEFFICIENT: A CRITICAL SURVEY

Harold Y. Wachman*

INTRODUCTION

A problem that currently confronts the engineer concerned with high-altitude flight involves the determination of drag coefficients for a vehicle in motion in a rarefied gas. The free-molecule drag coefficient, C_D , could, in principle, be readily computed if the vehicle were to receive from each incident gas molecule, upon collision, all the momentum that the molecule has relative to the vehicle, i. e. , if the incident gas molecules were brought to rest (ignoring thermal motion) relative to the vehicle's surface upon collision with it. However, this kind of molecular behavior is unusual. It is more likely that after a single encounter with a surface, gas molecules will, on the average, rebound from it with appreciable velocities. Therefore, if the gas about the vehicle surface is rarefied, molecules will escape the interface after surrendering to the surface, on the average, only a fraction of their incident relative momentum, and the drag coefficient will depend not only on the velocities of the incident molecules but also on the velocities of the ones rebounding.

In the case of artificial earth satellites the choice of a numerical value for the average speed of the incident molecules relative to the satellite surface, V_i , presents no special problem. At altitudes of less than 1000 miles, where the atmospheric density is sufficiently high to produce significant neutral particle

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drag, the satellite speed exceeds the mean thermal molecular speed by a factor of 6 or more⁽¹⁾. Hence V_i is, nearly enough, equal to the flight speed of the satellite. However, the mean speed of the rebounding molecules relative to the satellite, V_r , is not known a priori and, since relevant experimental data are not yet available, numerical estimates of free molecule drag coefficients often lack the required precision. For example, data obtained from observations of orbital decay of artificial satellites can be used to calculate the product of C_D and the atmospheric density. The fact that average values of the atmospheric density at high altitudes derived from these data are not very precise is due, in part, to the uncertainty in C_D . Harris and Jastrow⁽²⁾ obtained average densities using $C_D = 2.3 \pm 0.3$, a value near the mean of two C_D values (2.0 and 2.7) calculated on the basis of extreme assumptions regarding the nature of the interaction of gas molecules at the satellite surface.

Perhaps the simplest way of relating V_r to V_i is by means of the thermal accommodation coefficient α . The accommodation coefficient is a quantity which is used to express the efficiency of energy transfer between a gas and a boundary; its relation to the ratio V_r/V_i , and to C_D , will be discussed below. Experimental studies of thermal accommodation have been mostly concerned with gases at, or near, room temperature. Therefore, the applicability of available values of α to the calculation of hyperthermal free-molecule drag coefficients is quite uncertain. However, methods which have been employed to determine the thermal accommodation coefficient, and physical factors which have been found to influence its

magnitude and behavior are pertinent to all future studies. The literature selected for review here represents efforts which, in the writer's judgment, have contributed most to an understanding of the phenomenon of thermal accommodation.

THE THERMAL ACCOMMODATION COEFFICIENT

Kundt and Warburg⁽³⁾, in an effort to test Maxwell's⁽⁴⁾ hypothesis that gas viscosity is independent of density examined the effect of changing gas density on the damping of a vibrating disk. Over a wide range of densities the gas behaved as predicted, but at low densities viscosity appeared to decrease with decreasing density. Kundt and Warburg suggested that the interaction between a low density gas and the surface of a solid is incomplete, and proposed that a gas at low density "slides" or "slips" over a surface which is transmitting shear to it. Maxwell showed that the Kinetic Theory can account for the slip phenomenon if in the treatment of viscous flow it is assumed that a portion f of every unit area of solid surface "absorbs all the incident molecules, and afterwards allows them to evaporate with velocities corresponding to those in still gas at the temperature of the solid, while a portion $(1-f)$ perfectly reflects all the molecules incident upon it⁽⁵⁾." Maxwell's hypothesis implies that the energy of the molecules reflected by the portion $(1-f)$ is not altered during collision, and suggests a thermal analogue for the phenomenon of viscous slip, i. e. , a discontinuity of temperature at an interface shared by a low density gas and a solid which are at different temperatures. Smoluchowski⁽⁶⁾ verified the existence of the thermal phenomenon when he measured the heat conducted by hydrogen from a heated thermometer bulb and found that the energy interchange between hydrogen and a glass surface

is also incomplete. Smoluchowski's analysis is outlined in texts on the Kinetic Theory of Gases ^(7, 8).

In 1910 Knudsen started to consider in detail the phenomenon of molecular (as opposed to "molar") heat conduction. He treated the problem somewhat as follows ⁽⁹⁾: Consider the process of incomplete energy exchange between a gas at the temperature T_g and a solid at T_s ; say, $T_s > T_g$. The average energy flux through the surface of the solid is the difference between the energy brought up by an incoming molecular stream and the energy carried away by a receding stream. The two streams may be considered independently if the gas density is very low. Accordingly, if the mean energy per molecule in the incoming stream is ϵ_g (corresponding to T_g) and N is the number of such molecules striking unit surface area per second, then the incident flux of energy is $N\epsilon_g = E_g$. Since the interaction is incomplete the mean energy of a molecule in the receding stream, ϵ_r , may be considered to be the same as the mean energy of a molecule issued from a body of gas at some temperature T_r whose value lies between T_s and T_g . The energy carried away from unit surface area per second is thus $E_r = N\epsilon_r$, [since there is no accumulation of gas at the surface N (incoming) = N (receding)] and the energy flux through the surface of the solid is $E_r - E_g$. If the interaction were complete, i.e., if the receding stream were to carry the same mean energy per molecule, ϵ_s , as does a stream issuing from a gas in equilibrium at the surface temperature T_s , then the energy flux through the surface would be $E_s - E_g$, where $E_s = N\epsilon_s$. These two energy differences suggest that the average efficiency of the energy exchanged, per collision, between a gas and a solid at their interface could be expressed as a coefficient of accommodation, α , defined by,

$$\alpha = \frac{E_r - E_g}{E_s - E_g} \quad (1)$$

Knudsen himself defined α in terms of the temperatures of the molecular streams as a measure of the extent to which gas molecules which strike and rebound from the surface of a solid accommodate themselves to the temperature of the solid. His formula⁽⁹⁾,

$$\alpha = \frac{T_r - T_g}{T_s - T_g} \quad (2)$$

can be obtained from Equation (1) by setting, in general, $E = N (2kT)$ where k is the Boltzmann constant and $2kT = \epsilon$, is the mean translational energy per molecule issued from a body of gas in equilibrium at the temperature T .

In presenting the derivations of Equations (1) and (2) we have accepted the assumption that the energy E_r carried by the receding molecular stream is the same as the energy carried by a stream issued from a body of gas at a definite temperature T_r . There is some doubt regarding the validity of this assumption. However, since E_r is a numerical quantity it can nevertheless be expressed as $E_r = N (2kT_r)$ where T_r is not a temperature but a parameter whose value lies between T_s and T_g ⁽¹⁰⁾. Alternatively, if α is determined under conditions such that the temperature difference $T_s - T_g = \Delta T$ vanishes, the assumption that T_r stands for the temperature of the receding stream becomes acceptable. Accordingly, Jackson and Mott⁽¹¹⁾ and Jackson and Howarth⁽¹²⁾ employed the definition:

$$\alpha = \lim_{\Delta T \rightarrow 0} \left(\frac{T_r - T_g}{\Delta T} \right) \quad (3)$$

Subsequent studies, which are cited below, suggest that within the range studied the magnitude of α is independent of ΔT . Therefore the modification introduced by Equation (3) may be unnecessary.

THE RELATION BETWEEN THE ACCOMMODATION COEFFICIENT AND THE FREE-MOLECULE SATELLITE DRAG COEFFICIENT

Shamberg's⁽¹⁾ analytical formulation of the hyperthermal free-molecule drag coefficient, C_D , will serve to illustrate the general relation between C_D and α . The term "hyperthermal" refers to the fact that the random, thermal, motion of gas molecules is neglected in the analysis on the assumption that the speed of the vehicle is several times (6 or more) greater than the mean thermal speed. The model consists of a uniform parallel beam of molecules that strikes a flat elemental surface at an angle of incidence θ_i and is then reflected as a conical or wedge-shaped beam having a half-angular width ϕ_o and an axis which is inclined at an angle θ_r to the plane of the surface, Figure 1. Taking all molecular speeds relative to the surface of the vehicle, the speed of the molecules in the incident parallel beam is V_i (which is the flight speed of the vehicle), and the speed of the molecules in the reflected conical beam is V_r . In order to characterize the dependence of θ_r upon θ_i Shamberg chose the relation

$$\cos \theta_r = (\cos \theta_i)^\nu, \quad \nu \geq 1 \quad (4)$$

In terms of these parameters the hyperthermal free-molecule-drag coefficient for all geometries is expressed by Shamberg as:

$$C_D = 2 \left[1 + \frac{V_r}{V_i} f(\nu, \text{shape}) \right] \quad (5)$$

The second term inside the brackets represents the contribution of the momentum of the rebounding molecules to the drag on the body. This term can be positive or negative depending on whether the molecules rebound in the direction of flight or in the opposite direction, respectively. The effective average direction of the rebounding molecules is taken into account by the factor $f(v, \text{shape})$, where "shape" refers to the contribution of the body shape, and v comes from the reflection law postulated in Equation (4). The ratio V_r/V_i is related by Shamburg to the thermal accommodation coefficient somewhat as follows: if η is the rate at which gas molecules collide with unit surface area, and m the mass of a molecule then, in general, $E = 1/2 \eta m V^2$. Considering a process during which each molecule makes only one collision with the surface, applying Equation (1) and using the notation introduced in this section he obtains,

$$\alpha = \frac{V_r^2 - V_i^2}{V_s^2 - V_i^2} \quad (6)$$

Since V_s , the speed of the satellite, is zero in the chosen reference frame

$$\frac{V_r}{V_i} = (1 - \alpha)^{1/2} \quad (7)$$

and
$$C_D = 2 \left[1 + \delta(\phi_0) (1 - \alpha)^{1/2} f(v, \text{shape}) \right] \quad (8)$$

The following are some general inferences drawn in Reference (1) from a parametric study of Equation (8) regarding the drag coefficient for a satellite in the free-molecule regime: (1) The drag coefficient is generally more sensitive to changes in the nature of the interaction between the gas molecules and the surface of the satellite than it is to the geometry of the satellite. (2) The drag

coefficient is more sensitive to changes in accommodation coefficient than it is to changes in the mean direction of the rebounding molecules. (3) Without accurate knowledge regarding the magnitude of the accommodation coefficient the detailed composition of the upper atmosphere may be neglected in estimates of satellite drag.

EXPERIMENTAL METHODS FOR DETERMINING THE ACCOMMODATION COEFFICIENT.

There are two important methods for determining thermal accommodation coefficients. About two-thirds of the reported values have been obtained by Knudsen's low-pressure method, the remaining one-third by the temperature-jump method⁽¹³⁾. In the application of either method the experimental cell usually consists of a fine wire filament of radius r_1 mounted axially in a cylindrical tube of radius r_2 , ($r_1 \ll r_2$). The filament is maintained at a constant temperature T_g by passing a small electric current through it, and the tube with filament mounted is immersed in a bath kept at a constant temperature T_w . The experimental gas contained in the tube is at a pressure < 0.05 mm when utilizing the low pressure method and roughly in the range 10 - 100 mm when utilizing the temperature-jump method. The difference, in principle, between the two methods is in the manner by which the energy of the incident molecular stream E_g , is determined. This energy can be known in a simple way only if it can be identified with the energy carried by molecules issued from a body of gas at a definite temperature. In the low pressure method molecular mean-free-paths are large enough relative to the relevant dimensions of the components of the cell that gas molecules transporting energy from the heated filament to the tube

walls can achieve thermal equilibrium with the tube walls at T_w before returning to the filament, or before making collisions with other gas molecules or with each other. Furthermore, as a result of the cylindrically symmetric cell geometry, and the fact that $r_1 \ll r_2$, the number of molecules which at any given time may find themselves in the receding stream moving from the filament to the tube walls with excess energy acquired at the filament is a very small fraction of the total number of molecules in the cell. (This fraction can be shown to be, roughly $r_1 \sqrt{T_g} / r_2 \sqrt{T_r}$ when the mean free path is $\geq (r_2 - r_1)$). Consequently the entire body of gas in the tube may be considered to be at the temperature, T_w , of the tube walls, thus $T_g = T_w$. At the gas pressures utilized for the temperature-jump method the conduction of heat from filament to tube walls induces temperature gradients in the gas and the assumption $T_g = T_w$ is not valid. Instead the method relies on a relation between the accommodation coefficient and the temperature jump distance; the latter quantity is determined from experimental measurements.

The detailed experimental procedure employed varies from laboratory to laboratory, however, the following is common in many investigations with either method. After the experimental tube is joined to a vacuum system it is surrounded by a bath kept at a constant temperature, T_w , and evacuated. The gas under investigation is introduced into the tube at the desired pressure and the filament is heated electrically. The current required to maintain the filament at an average temperature, T_s , and the potential drop across the filament are measured, and these data are used to calculate the power input to the filament W_f , and its resistance. The average temperature of the filament is calculated

accurately from its resistance and the temperature coefficient of resistance of the material. W_f , the total power required to maintain the filament at T_s , is equal to the power which the filament loses by radiation, end conduction to the supports, and gas conduction. The power lost by radiation and end conduction is, approximately, W_v , the power which the filament kept at T_s would lose in vacuum. Therefore, W_v is also measured and its value subtracted from W_f to obtain W_g , the net steady state power loss from unit filament area to gas.

A. The Low-Pressure Method

The accommodation coefficient is computed using an expression introduced as a definition for α by Blodgett and Langmuir⁽¹⁴⁾;

$$\alpha = \frac{W_g}{W_{KT}} \quad (9)$$

where $W_{KT} = E_s - E_g$ is the free molecule heat conductivity calculated from the Kinetic Theory as follows: As shown above, E in general may be expressed as,

$$E = 2 N k T \quad (10)$$

The Kinetic Theory expression for, N , the number of molecules striking (or rebounding from) unit filament area per second is

$$N = n \bar{c} / 4 \quad (11)$$

where n is the molecular number density and $\bar{c}$ the average molecular velocity, (both quantities are referred to a gas at T_g). Converting to molar quantities with R as the molar gas constant, A Avogadro's number, M the molecular weight of the gas, and using the relations $n = AP/RT_g$ and $\bar{c} = (8RT_g/\pi M)^{1/2}$, W_{KT} becomes

$$W_{KT} = \frac{P}{\sqrt{2 \pi M R T_g}} 2 R (T_s - T_w), \quad (T_g = T_w) \quad (12)$$

The quantity $2R$ is the translational molar heat capacity of a molecular stream (it is greater than the corresponding quantity for still gas by $R/2$). A more general expression is obtained by replacing $2R$ by $C_v + R/2$ where C_v is the molar heat capacity at constant volume. Incorporating this into Equation (12) and using $\Delta T = T_s - T_w$ and rearranging results in ⁽¹⁵⁾;

$$\frac{W_{KT}}{P \cdot \Delta T} = \Lambda = \left(\frac{C_v}{R} + \frac{1}{2} \right) \sqrt{\frac{R}{2 \pi M T_g}} \quad (13)$$

Values of Λ , the free-molecule heat conductivity per unit ΔT unit pressure and unit filament area, for several gases at 30°C are listed in Ref. (15).

B. The Temperature-Jump Method

Kennard ⁽⁷⁾ has outlined the temperature-jump method in the form applied by a majority of modern investigators. The method utilizes measurements of the thermal conductivity of a gas at a series of pressures which lie in a range within which the conductivity should be independent of pressure. However, the measured conductivity appears to diminish with decreasing pressure due to the pressure dependence of the temperature discontinuity at the gas boundaries. In computing accommodation coefficients from temperature-jump data obtained in cells of cylindrical symmetry the temperature discontinuity at the tube walls may be neglected ⁽¹³⁾. The accommodation coefficient is related to the temperature-jump distance at the filament, g_s , by ⁽⁷⁾ ⁽¹³⁾:

$$\frac{2-\alpha}{\alpha} = \frac{g_s P}{K_{T_e}} \left(\frac{C_v}{R} + \frac{1}{2} \right) \left(\frac{2 R}{\pi M T_e} \right)^{1/2} \quad (14)$$

where K_{T_e} is the (true) thermal conductivity of the gas at the temperature T_e , and T_e (Kennard's T_k) is the temperature that would obtain in the gas at the

filament surface if the temperature gradient $(dT/dr)_r$ which exists in the body of gas at a distance r from tube axis were to continue in regular functional relation to r right up to the filament itself ($r = r_1$). The temperature-jump distance g_s is obtained as follows: The temperature discontinuity $T_s - T_e$ is related to g_s by the Poisson temperature-jump equation:

$$T_s - T_e = -g_s \left(\frac{dT}{dr} \right)_{r=r_1} \quad (15)$$

Smoluchowski⁽¹⁶⁾ showed that g_s is inversely proportional to the gas pressure; thus the product $g_s P$ in Equation (14) is often replaced⁽¹⁷⁾ ⁽¹³⁾ by g'_s which is independent of pressure. The heat conducted in a cylindrical cell per unit filament area per second, W_g , is obtained by combining the Poisson expression with the Fourier heat conduction equation to give⁽⁷⁾ ⁽¹³⁾:

$$\frac{W_g}{\Delta T} = \gamma = \frac{\bar{K}}{r_1 \ln(r_2/r_1) + g'_s/P} \quad (16)$$

where $\bar{K}$ is the thermal conductivity at some temperature between T_s and T_w . Experimental measurements determine T_s and T_w , and W_g as a function of P . In the modern work which begins with Dickins⁽¹⁸⁾ $1/\gamma$ is plotted against $1/P$ to obtain a straight line according to Equation (14) of the form $y = mx + b$, with slope $m = g'_s/\bar{K}$ and intercept $b = (r_1/\bar{K}) \ln(r_2/r_1)$. The value of $\bar{K}$, determined from the intercept, when multiplied by the value of the slope gives g'_s .

A computation of α by Equation (14) also requires an estimate of T_e and K_{T_e} . Thomas and Golike⁽¹³⁾ proceeded as follows: Setting $g_s P = m \bar{K}$ they obtain:

$$\frac{2 - \alpha}{\alpha} = m \frac{\bar{K}}{K_{Te}} \left(\frac{C_v}{R} + \frac{1}{2} \right) \left(\frac{2R}{\pi M T_e} \right)^{1/2} = \beta m \quad (17)$$

Within a narrow temperature range K , in general, is proportional to T^a where a is a constant whose value depends on the gas. The temperature $T_{\bar{K}}$ at which $\bar{K}$ is the conductivity is found to be (for He, Ne and CO_2) very close to the mid-temperature of T_e and T_w ; i. e. $T_{\bar{K}} = T_w + \Delta T_e / 2$ where $\Delta T_e = T_e - T_w$. With these relations β in Equation (15) becomes:

$$\beta = \frac{\left(T_w + \frac{\Delta T_e}{2} \right)^a}{\left(T_w + \Delta T_e \right)^{a + 1/2}} \left(\frac{C_v}{R} + \frac{1}{2} \right) \left(\frac{2R}{\pi M} \right)^{1/2} \quad (18)$$

The quantity ΔT_e is approximated as ΔT ⁽¹³⁾. This approximation is better for Ne than for He and best for CO_2 .

C. Comparison of the Methods

The low-pressure method is based on a theory which becomes quite accurate at very low pressures. Experimental results which are cited in subsequent sections demonstrate that when the experimental details are properly attended the low pressure method gives reproducible results which are consistent from laboratory to laboratory.

The temperature jump method is not as well founded. Theory relating α to g_s is subject to some uncertainty and Equation (14) is only an approximate relation between these quantities ⁽⁷⁾. Grilly, Taylor and Johnston ⁽¹⁷⁾ do not consider α obtained by Equation (14) to be the same as the Knudsen low-pressure accommodation coefficient. They write: "A theoretical relation between g'_s and Knudsen's accommodation coefficient has not as yet been obtained and probably no simple relation between them exists, because of the complex nature of the

actual stream of incident molecules⁽¹⁷⁾. They define the quantity α of Equation (14) not as the accommodation coefficient but a slightly different coefficient which they name the "Maxwell-Knudsen" accommodation coefficient. There is, in fact, very poor agreement between the two methods on the basis of comparison of published values of accommodation coefficients⁽¹³⁾ and until recently the ability of the two methods to give the same α value was questionable. In 1954 Thomas and Golike⁽¹³⁾ published the results of a comparative study of the accommodation coefficients of He, Ne and CO₂ on platinum by the two methods. Most of the modern temperature-jump work is on Pt^{(18) (19) (20) (21) (17) (13)}. The comparison was made using the same tube and vacuum system, with gases from the same reservoir and purification system. Within the limitations imposed by the requirements of the methods, experimental procedures and conditions were maintained the same. Agreement with He and CO₂ was very close. For Ne the results were ambiguous, but the discrepancies (which were of the order of 25%) were associated with consistent failure to reproduce the same surface conditions rather than with failure of the temperature-jump method.

EXPERIMENTAL PROCEDURES

A. Determination of the Power Loss in Vacuum

Because the temperature distribution along a filament is altered by gas conduction⁽¹⁵⁾ the measured power loss from a filament in vacuum, W_v , is not exactly equal to the radiation and end-conduction losses from a filament surrounded by gas. When ΔT is small the altered distribution induces only a small change in the radiation loss, the principle change being in end losses

arising from new temperature gradients at the filament ends. For example, for a 5 mil potassium covered tungsten filament 20 cm in length operated at $\Delta T \simeq 10^\circ\text{C}$, $T_w \simeq 300^\circ\text{K}$, neglecting to correct for the change in end losses results in an error of + 14% in the accommodation coefficient of helium⁽²²⁾. Attempts to minimize or correct the error have, in general, been successful. One approach is to use power loss data obtained from the central segment of the filament only where changes in gradients with gas conductions are diminished. For example, Thomas and Olmer⁽¹⁵⁾ and also Thomas and Brown⁽²³⁾ attached potential leads at a distance from each end of the filament and measured the power input to the central segment alone. Thomas and Schofield⁽²⁴⁾ using a single potential lead subtracted the appropriate measurements taken on the shorter section from those obtained on the longer section to obtain net values which apply to the middle section. A more elegant approach was taken by Thomas and his co-workers⁽¹³⁾, ⁽¹⁵⁾, ⁽²³⁾ when, with auxiliary heaters, they supplied heat at a controlled rate to the filament ends and thus obtained a flat temperature distribution over the entire length of the filament. In addition to these, R. E. Brown developed an analytical method for filament end-loss correction which is reproduced in Appendix A to a dissertation by H. L. Petersen⁽²²⁾.

B. Preparation of the Experimental System

The magnitude of the accommodation coefficient may be markedly affected by gaseous layers adsorbed on the filament surface formed sometimes quite slowly from traces of impurities in the vacuum system or from the gas under consideration. In order to subject these effects to reproducible control rigorous

experimental procedures must be adopted. J. K. Roberts ⁽²⁵⁾ was the first to recognize this need and his pioneering work which began in 1930 is the basis of all modern investigations. However, many workers who followed Roberts have not adopted the required procedures and made no serious attempt to create or maintain solid surfaces of known composition. As a result, many published values of accommodation coefficients cannot be associated with the interaction of known gases on known surfaces, and values for presumably the same gas and surface may be widely different. Compare, for example, the accommodation coefficient values of helium on tungsten of 0.0165 reported by Thomas and Schofield ⁽²⁴⁾ and about 0.5 obtained ⁽²⁶⁾ on uncleaned tungsten. The lower value was obtained after the vacuum system, experimental tube, and filament were all subjected to careful outgassing and the tube walls covered with an evaporated aluminum film to act as getter. This value is very probably characteristic of the accommodation coefficient of helium on tungsten. The value 0.5, however, cannot be associated with a known surface.

It may be that a clean metal surface can be maintained only in the presence of a few gases, helium and neon for example. However, even when the gas under investigation itself adsorbs on the surface, the surface should be initially clean since the magnitude of α may depend on the type and quantity of adsorbed gas. Wachman ⁽²⁷⁾ found, for example, that the value of α for hydrogen on tungsten initially covered with oxygen is appreciably different than α for hydrogen measured on initially clean tungsten; hydrogen was presumably adsorbed on both bare and oxygen covered surfaces during the measurements.

The problem of producing and maintaining a clean surface is not an easy one since such a surface is very reactive and rapidly acquires an adsorbed layer

even when exposed to a good vacuum (say 10^{-10} mm of Hg). Therefore the experimental system must be treated to reduce the quantity of residual gaseous impurities to a level at which the filament surface, once cleaned, remains essentially free of impurities during the course of a run. Thomas and Schofield ⁽²⁴⁾ proceeded as follows: "The system was all Pyrex with two mercury condensation pumps in tandem, with no stopcocks in the high vacuum line, but with several special grind mercury seal stopcocks in the gas supply and purifying system, which was separated from the main system at all times by a mercury cut-off except during preliminary evacuation and admission of gas." They describe the outgassing procedure as follows ⁽²⁴⁾: "Ovens are then placed about the tube, charcoal trap on the gas supply manifold and liquid air trap. These are baked at about 400°C for several hours, open to the pumps. With the ovens hot, the rest of the system is then heated repeatedly with a large brush gas-air flame for two to three hours, almost to the softening point of the glass, with special attention devoted to the region between the liquid air trap and the tube. After cessation of flaming, the ovens are turned off, liquid air is put on the single U-tube on the mercury side of the trap, and the filament is heated to flashing temperature."

Apart from the problem of preparing the experimental system the filament surface itself must be cleaned. Roberts ⁽²⁵⁾ outgassed tungsten filaments by heating to 2000°C . However, this procedure can be applied only to a few metals. The oxide coating which covers most metal surfaces is, in most cases, not volatile below the metal's melting point. Eggleton and Tompkins ⁽²⁸⁾ successfully reduced the oxide coating on an iron filament by heating in hydrogen, but found that the process left a hydrogen film on the surface which could not be

desorbed by prolonged heating in vacuum. To obtain a clean iron surface they bombarded the filament with ions of nitrogen and argon after the hydrogen reduction. Faust⁽²⁹⁾ working with aluminum attempted to form a clean surface by evaporating aluminum onto platinum and tungsten filaments, Brown⁽¹⁰⁾ applied this technique to form clean beryllium surfaces, and Petersen⁽²²⁾ to the determination of accommodation coefficients on clean sodium and potassium.

RESULTS OF EXPERIMENT

The work described in subsequent sections was by the low-pressure method unless otherwise specified.

A. Effects of the Surface on the Thermal Accommodation Coefficient

Experimental investigations in which serious attempts were made to work with surfaces of known composition begins with Roberts⁽²⁵⁾. He measured accommodation coefficients of helium⁽³⁰⁾ and neon⁽³¹⁾ on cleaned tungsten and obtained values which were roughly one-fifth the lowest previously reported. Before each run Roberts outgassed the surface by heating and during each run the helium and neon were continuously circulated through charcoal at the temperature of liquid air to remove adsorbable impurities coming from the glass walls of the apparatus. Mann⁽³²⁾, working with helium, and Mann and Newell⁽³³⁾ with hydrogen and deuterium on platinum also attempted to clean the surface. However, they did not purify the gases they used and contaminants carried by these adsorbed rapidly on the filament.

Roberts' values for the accommodation coefficient of helium on tungsten, $\left[\alpha (\text{He} - \text{W}) \right]$, at 300° K lie between 0.05 and 0.06, while values on untreated tungsten surfaces lie about 0.3. The fact that the accommodation coefficient

increases with adsorption on a surface was confirmed by Mann⁽³²⁾, but questioned by Bremner⁽³⁴⁾ who ascribed the increase of α with time, observed by Roberts, to persistence of thermal effects of flashing. However, Roberts' observations of the behavior of α were reconfirmed by Eggleton, Tompkins and Wanford⁽³⁵⁾ and by J.W. Faust⁽²⁹⁾. Faust, working with inert gases on evaporated aluminum surface found that low α values can be obtained on platinum and tungsten filaments kept hot during the evaporation of aluminum from other filaments to the tube walls. Apparently the aluminum coating on the tube walls was acting as a getter, thus maintaining a lower pressure of impurities in the tube than could be obtained with the vacuum pumps alone. Thomas and Schofield⁽²⁴⁾ improved this technique and applied it to measurements of α (He - W) from 83° to 303°K. In all previous attempts to obtain clean-surface α values, the measured α increased rapidly with time after flashing the filament. The increase with time was caused by adsorption of gaseous impurities not entirely eliminated from the experimental system. To obtain clean surface values, Roberts plotted α vs. time after flashing and extrapolated to zero time. In the work of Thomas and Schofield the change with time was almost entirely eliminated, and the measured values of α (He - W), about 0.0165, were lower than any reported before. Silvernail⁽³⁶⁾ virtually eliminated the change with time using a mischmetal getter in an investigation of α (He, Ne, A - W) from 77° to 303°K.

The use of a getter on the tube walls appears an excellent way to supplement the general precautions required to obtain α values of inert gases on clean surfaces. However, the getter technique for removing adsorbable impurities is impractical when the gas whose α is being measured itself adsorbs on the getter. When this is the case, satisfactory vacuum conditions may be obtained by

prolonged and careful outgassing [see, for example, Footnote (7) Reference (24) and also Reference (27)] .

In 1935 Roberts⁽³⁷⁾ suggested that the accommodation coefficient of an inert gas such as neon may be used as an indicator for adsorption of other gases. He proceeded to investigate the adsorption of hydrogen⁽³⁷⁾, oxygen⁽³⁸⁾ and nitrogen⁽³⁹⁾ on initially clean tungsten by observing change in the accommodation coefficient of neon. Figure (2) is an example of the data he obtained. The Figure shows plots of α (Ne) at two temperatures vs time (after flashing) and illustrates the change in α (Ne) caused by the admission of small quantities of hydrogen to the experimental tube. A summary of Roberts' work is contained in his book⁽⁴⁰⁾, and in the revised edition by Miller⁽⁴¹⁾. Others following Roberts have applied the accommodation coefficient method with neon to study adsorption on initially bare tungsten. Thus Van Cleave⁽⁴²⁾ studied adsorption of nitrogen, and Morrison and Roberts⁽⁴³⁾⁽⁴⁴⁾ investigated adsorption of oxygen. Wachman⁽²⁷⁾ using helium as an indicator gas investigated adsorption of H_2 , D_2 , O_2 , N_2 , CO_2 , CH_4 , C_2H_4 and C_2H_6 . Eggleton and Tompkins⁽²⁸⁾ applied the method to an investigation of adsorption of H_2 , O_2 and N_2 on initially clean iron, and Petersen⁽²²⁾ to a study of adsorption of potassium on tungsten. The remarkable dependence of the accommodation coefficient on the species of gas adsorbed on a surface is illustrated by the difference between α (He) values found on hydrogen and deuterium covered tungsten. Wachman⁽²⁷⁾ starting with a value of 0.0200 for α (He) on bare tungsten measured 0.0407 for α (He) on hydrogen covered tungsten as against 0.0458 on deuterium

covered tungsten. In addition $\alpha(\text{H}_2)$ and $\alpha(\text{D}_2)$ were also found to have different values on surfaces of hydrogen and deuterium, respectively, adsorbed on initially bare tungsten.

The magnitude of the accommodation coefficient depends not only on the condition but also on the type of surface. Tungsten is preferred in many investigations because it can be obtained in fine filament form and is readily outgassed by heating. These properties of tungsten have, in part, also been responsible for its extensive use in studies of various surface phenomena by other methods since the earliest work of Langmuir, ⁽⁴⁵⁾ ⁽⁴⁶⁾. This coincidence is convenient in interpreting results of experimental and analytical investigations on accommodation coefficients. There is at the same time, and partially for the same reasons, an extensive bibliography on platinum. Most of the temperature jump work, for example, is with platinum (see above). However, in most studies with platinum little effort was made to rid the system of adsorbable impurities. The work of Thomas and Brown ⁽²³⁾, though not achieving the excellent conditions obtained in later work with tungsten ⁽²⁴⁾, ⁽³⁶⁾, may be cited as an exception. The measurements were with He, Ne, Ar, Kr, H₂, N₂, O₂, CO, and Hg on platinum.

Table I presents a list of accommodation coefficient values of helium and neon on different surfaces at about room temperature. The table includes mention of the method used to prepare each final surface and the reference. The values in the table are, in our opinion, among the most reliable ones available.

Table I

Accommodation Coefficients of Helium and Neon on

Clean Metal Surfaces

<u>Gas</u>	<u>Metal</u>	<u>Preparation of Surface</u>	<u>Accommodation Coefficient</u>	<u>Ref.</u>
Helium	Tungsten	flashing	0.017	(24), (36)
Neon	Tungsten	flashing	0.042	(36)
Neon	Iron	Reduction with H ₂ and ion bombardment	0.056	(28)
Helium	Platinum	flashing	0.038	cited in (10)
Helium	Aluminum	Evaporation on platinum	0.073	(29)
Neon	Aluminum	Evaporation on platinum	0.159	(29)
Helium	Beryllium	Evaporation on tungsten	0.145	(10)
Neon	Beryllium	Evaporation on tungsten	0.315	(10)
Helium	Potassium	Evaporation on tungsten	.083	(22)
Neon	Potassium	Evaporation on tungsten	0.199	(22)
Helium	Sodium	Evaporation on tungsten	.090	(22)
Neon	Sodium	Evaporation on tungsten	.198	(22)

The following is a brief list of references (n. v.) to measurements of α on surfaces which may or may not have been characteristic of the bare material:

α (He - Ni), ⁽⁴⁷⁾; α (Hydrocarbon molecules - Ni), ⁽⁴⁸⁾; α (H₂ - Fe), ⁽⁴⁹⁾;
 α (He, Ne, H₂, N₂ - glass) ⁽⁵⁰⁾ ⁽⁵¹⁾; α (air - several engineering surfaces), ⁽⁵⁰⁾.

B. The Temperature Dependence of the Accommodation Coefficient

The simplest way of studying the effect of temperature on the accommodation coefficient is with a clean surface. A gas covered surface usually changes in composition with changing surface temperature and may also change with changing gas temperature. Therefore, observed changes in α , with temperature, on a gas covered surface may be due to changes in surface composition. An interesting collection of data is presented by Thomas and Olmer ⁽¹⁵⁾ who assembled, in a single graph, measured values of α vs. T from several sources [see also page

129 Reference (8)]. All the data cited, with one exception, show α decreasing with increasing temperature below 500°K. The exception is a plot of Roberts' (30) values of α (He) on cleaned tungsten which shows α increasing with temperature. It appears a good assumption that in all the work cited [except Reference (30)] the surface at each temperature was saturated with adsorbed gas. Since the (saturation) quantity of gas on a surface usually decreases with increasing temperature the corresponding α values would also decrease. The surface in Reference (30), however, was partially clean, with surface population certainly below the saturation value. In this case, an increase in T_g (say, at constant ΔT) may have increased the rate at which contaminant gas from the tube walls ($T_g = T_w$) arrived at the partially covered filament surface and α increased because the surface contamination increased. Evidently none of these data offers much insight into the temperature dependence of the accommodation coefficient.

The accommodation coefficient may depend on both T_s and T_g (or, more conveniently on T_g and ΔT). Among the most reliable investigations of this dependence are the studies described in References (24) and (36) of accommodation coefficients of inert gases on clean tungsten. Figure 3 is a plot of α (He) vs. bath temperature, T_w , ($T_g = T_w$) according to (24), (curve B), and according to (30), (curve A). Curve B values were with ΔT nearly constant at about 18°; the change of α (He) with T_w is sensible but small with values 0.0151 at -190°C, 0.0162 at -135° and -80°C, 0.0172 at -30°C and 0.0167 at 30°C. Silvernail (36) (not shown) found α (He) 0.016 at 30°C and 0.012 at -196°C. The change in α (Ne) (36), with T_w is somewhat more marked in the same temperature range exhibiting a slight minimum at -180°C. Figure 4, (24), is a plot of α (He) values

against time after the filament was outgassed by flashing. The results of two runs are plotted with $T_w = -190^\circ\text{C}$ and T_g changing at intervals shown on the plots; thus the plots show the effect of changing ΔT (at constant T_g) on the magnitude of α (He). These results combined with other from Reference (36) indicate that for He and Ne on clean tungsten α is nearly constant with changing ΔT , and changes with T_w at constant ΔT .

C. The Effect of Gas Pressure on the Accommodation Coefficient

Since surface composition may be altered by changing ambient gas pressure the accommodation coefficient may appear to change with pressure. However, the accommodation coefficient defined as a measure of the efficiency of the energy exchanged, per collision, is by definition independent of pressure. This behavior with pressure is indeed found when adequate care is taken to maintain constant surface composition in the course of experiment.

Amdur, Jones and Pearlman⁽⁵³⁾ reported that the accommodation coefficients of several gases including He, Ne, Ar, Kr and Xe on platinum at room temperature changed with pressure below 0.1 mm Hg. Amdur⁽⁵⁴⁾ attributed this pressure dependence to simple Langmuir adsorption on the surface, of the gases whose α was being measured. Morrison⁽⁵⁵⁾ accepted this interpretation for H_2 , D_2 , N_2 , CO and O_2 but offered an alternative one for the pressure dependence observed with the inert gases. These were about 99.9% pure and Morrison suggested that the impurities carried by these were of sufficient quantities to cause the observed effect. Thomas and Brown⁽²³⁾ measured the accommodation coefficients of the gases used by Amdur et. al.⁽⁵³⁾ on platinum as a function of

pressure but attempted to maintain the composition of the surface constant by designing the experiments to minimize and control the quantities of adsorbable impurities in the experimental system. Some of their results are shown as plots in Figures 5 and 6. These show that the accommodation coefficients of the nine gases are essentially constant with pressure in the pressure range where the low-pressure method is applicable. The lower values at higher pressure in Figure 5 are not real values of α , but were included to show for each gas (and experimental tube) the range of application of the low-pressure method.

Harnett⁽⁵⁶⁾ criticized the manner by which the low-pressure method has been applied by a majority of the investigators. He writes: "To summarize, an accurate measurement of the accommodation coefficient using a thin heated wire in a cylindrical enclosure must satisfy the following requirement: . . . (2) The pressure level within the enclosure should be low enough to ensure that the mean-free-path (λ) is at least three times the radius (r_o) [our r_2] of the outer cylinder, $\lambda > 3 r_o$. (3) The pressure level within the enclosure should be high enough to ensure that the radiation heat transfer (Q_R) does not overwhelm the conduction contribution (Q_C), say $Q_R/Q_C < 1$ or 2. It is clear that these [(2) and (3)] are conflicting requirements and not many investigators have taken full cognizance of them." The objection (2) is taken in failure to appreciate the logic of Knudsen's low-pressure method. Briefly, Knudsen's argument is somewhat as follows: The molecules which at any instant make up the gas about a mean-free-path λ from the wire are those that come from the body of gas and those that come from the wire. Those that come from the body of gas are brought up to a cylinder of unit length a radial distance λ from wire at a rate about $\frac{n\bar{c}}{4} (2\pi\lambda^2)$; those coming

from unit length of wire do so at the rate with which they strike unit length of wire, $\frac{nc}{4} (2 \pi r_1)$. Hence, of all the molecules which make up the gas at a distance λ from the wire the fraction r_1/λ come from the wire carrying excess energy acquired at the wire. When this fraction is small, say $r_1/\lambda \leq 0.05$, the properties of the gas at λ are practically uninfluenced by the presence of the wire. Furthermore, since the molecules arriving at the wire have also had their last collision at about λ , the molecules arriving at the wire are essentially uninfluenced by those returning. Consequently when using cells of cylindrical geometry the applicability of free-molecule heat conduction theory is tested by the ratio λ/r_1 proposed by Knudsen rather than λ/r_2 suggested in Reference (56). This is verified by the experimental data in Reference (23). Consider the α (Kr) and α (A) values obtained by Thomas and Brown at $\Delta T = 100^\circ \text{C}$ in tube B, with $2r_1 = 0.0127 \text{ cm}$ and $2r_2 = 1.95 \text{ cm}$. Using λ (Kr) = $3.69 \times 10^{-3} \text{ cm}$ and λ (A) = $4.71 \times 10^{-3} \text{ cm}$ at 273°K and 1 mm of Hg we computed the Knudsen numbers $\text{Kn}(1) = \lambda/2r_1$ and $\text{Kn}(2) = \lambda/2r_2$, relative to wire and tube diameters, respectively. These are tabulated in Table II with several α values given in Table II of Reference (23).

Table II

Accommodation Coefficients of Krypton and Argon on Platinum at $T_W = 305^\circ \text{K}$, $\Delta T = 100^\circ$ according to Thomas and Brown with Corresponding Knudsen Numbers.

α (Kr)	Kn(1)	Kn(2)	α (A)	Kn(1)	Kn(2)
.699	84	0.55	.649	69	0.45
.686	74	0.48	.648	46	0.30
.689	54	0.35	.649	30	0.19
.705	43	0.28	.649	16	0.10
.689	32	0.21	.640	12	0.064
.693	26	0.17			
.703	21	0.14			
.665	11	0.073			
.634	6	0.038			

It is clear from the table that as long as $Kn(1) > 10$, α calculated by the low pressure theory is essentially independent of $Kn(1)$. The table also shows the low pressure theory is applicable (for the given cell geometry) with $Kn(2)$ values about 1/10 the minimum suggested in Reference (56). This fact also renders Hartnett's objection (3) less serious; since one may work at gas pressures about 10 times, or more, greater than the maximum he suggests, it is possible to keep the ratio W_g/W_v (his Q_C/Q_R) at a sensible value. For example, with argon at $P = 0.02639$ mm, and $\Delta T = 100^\circ C$ ($Kn(2) = 0.10$) Thomas and Brown report W_g (filament area) = 0.0147217 watts and W_v (filament area) = 0.0048545 watts; thus $W_g/W_v = 3.0$ and $\alpha = 0.649$. At the lowest pressure reported (0.00604 mm) W_g would be about 0.23 of the above value and assuming the same W_v the ratio W_g/W_v is about 0.7. With this ratio α was also 0.649. It is to be noted that even when working with a gas such as helium having an accommodation coefficient considerably smaller than 0.65 reported for argon in (23) one seldom experiences difficulty in finding a convenient pressure range within which W_g is a significant fraction of the total power loss from the filament.

RESULTS OF THEORY AND ANALYSIS

Baule⁽⁵⁷⁾ reported the first attempt to calculate accommodation coefficients from known properties of a gas and a solid. He applied classical theory and used a model in which the gas and surface atoms behave like elastic spheres and have a Boltzmann distribution of energies. Baule supposed each gas atom to make

a single collision with a solid atom before rebounding, and applied the laws of conservation of energy and momentum to obtain for α the expression:

$$\alpha = \frac{2 m M}{(m + M)^2} \quad (20)$$

where m and M are the masses of the gas and surface atoms. In case the surface is rough and multiple collisions occur, say s in number, then according to Baule the apparent (or observed) accommodation coefficient, α_s is given by:

$$\alpha_s = 1 - \left[\frac{m^2 + M^2}{(m + M)^2} \right]^s \quad (21)$$

Equation (20) is derived in Reference (7). Equations (21) and (20) combined result in an expression identical in form with the formula given by Roberts (25) to account for the effect of surface roughness on measured α ; viz:

$$\alpha = 1 - (1 - \alpha_s)^{1/s} \quad (22)$$

Brown (10) compared the variation of the ratio $\alpha(\text{Ne})/\alpha(\text{He})$ with M predicted by Equation (21), with experimental data in somewhat the following way: Equation (21) may be written as $\alpha_s = s\alpha - \frac{s(s-1)}{2!}\alpha^2 + \dots$; and since $\alpha(\text{He})$ and $\alpha(\text{Ne})$ on clean metal surfaces are considerably less than unity the Equation (21) can be reduced to:

$$\alpha_s = s\alpha = 2 s m M / (m + M)^2 \quad (23)$$

Figure (7) according to Reference (10) shows a plot of $\alpha(\text{Ne})/\alpha(\text{He})$ vs. M computed from experimental data and from Equation (23) in which $s_{\text{Ne}}/s_{\text{He}}$ is taken as unity on the assumption that s depends only on the structure of the surface.

Hurlbut⁽⁵⁸⁾ outlined objections to the Baule model which are, in part, as follows: The choice of a classical model is questionable, and the assumption that each solid atom is in independent elastic suspension is not realistic. Experimental results suggest that a surface possesses greater effective mass in collision than possessed by any one surface atom. The assumption that the time of collision is infinitely short is also doubtful, especially at high interaction energies where an incident particle may penetrate below the surface of the lattice. In addition to these is the empirical fact that experimental values of α (He and Ne on W, for example) lead to fractional numbers of collisions with the surface, (Equation (21)) a result in conflict with reality.

Modern theory begins with Zener⁽⁵⁹⁾ and Jackson⁽⁶⁰⁾ et. al.⁽¹¹⁾, ⁽¹²⁾. The model is of gas atoms which have a one dimensional distribution of energies. The lines of motion of solid atoms and incident gas particles are assumed normal to the surface. The theoretical approach, in general, is to consider the solid atoms as oscillators which behave in the same way as atoms in the interior of the solid and compute the probability that a solid atom in vibrational state i struck by a gas atom with energy E will undergo a transition to state i' , the gas atom departing with energy $E + (i - i') h\nu$. Jackson and Mott⁽¹¹⁾ considered the energy exchange to be nearly always limited to a single quantum transition of the oscillator. The assumption is that when the interaction energy of a gas atom with the solid is expanded in powers of displacements of lattice atoms from their equilibrium positions only linear terms are important. Thus in the final formulas for α , $|i - i'|$ is always taken as unity. Strachan⁽⁶¹⁾ has justified this assumption

by showing that the probability of a solid changing a given amount of energy by a one-quantum jump is much larger than the probability of a change by a two quantum jump.

One important difference among the several approaches to theory is in the treatment of the solid. In the earlier theory the distribution of energy amongst the atoms of the solid is taken to be that of an assembly of oscillators all of the same frequency ν as in Einstein's specific heat theory. In later theory account is taken of the detailed distribution of normal modes within the crystal, i.e., the solid is treated in the same way as in the Debye specific heat theory. The accommodation coefficient, as defined by Equation (3), is calculated from the transition probability by averaging over the energies of the gas atoms and over the vibrational frequency distribution of the solid atoms. Jackson and Howarth⁽¹²⁾ indicate how this average may be performed.

Another important difference among theoretical treatments is in the assumptions regarding the interaction between gas atoms and solid surface. Jackson and Mott⁽¹¹⁾ considered two types of interaction: In one a one-dimensional repulsive exponential field was assumed, with potential energy at an interatomic distance y of the form $V = C e^{-ay}$, where C and a are constants; in the other a rigid elastic sphere model was treated; taking y_0 as the distance of closest approach of gas and solid atoms V was set at zero for $y > y_0$ and at infinity for $y < y_0$. In the latter case the expression for α does not contain adjustable constants; it results in a ratio $\alpha(\text{Ne}) / \alpha(\text{He})$ about 5 on the same metal surface while Roberts' values give 1.2 and more recent values about 2.3. Calculations

of α values as a function of temperature according to the theory (with $a = 9 \times 10^8 \text{ cm}^{-1}$) result in satisfactory agreement with the temperature dependence exhibited by Roberts' $\alpha(\text{He} - \text{W})$ values ⁽³⁰⁾. These three clean surface α values were the only ones available at the time the Jackson-Mott theory was developed.

The potential function Ce^{-ay} implies repulsion at all distances. It is known, however, that there is an attractive field between a solid and a gas (the fact that adsorption can take place is evidence that such a field exists). The attractive field is considerably greater for neon than it is for helium, and the theory described thus far is not applicable to experimental results with neon. Devonshire ⁽⁶¹⁾ in one of a series of papers by Lennard-Jones and his co-workers attempted to account for the attractive as well as the repulsive field by assuming an interaction potential in the form of a Morse potential function. In this form the interaction potential is attractive at large distances and repulsive at small ones with a minimum (potential well) in between. Devonshire did not treat the possibility that a gas atom may be entrapped in vibrational states in the potential well. However, the formulas for α which Devonshire derived are more general than previous ones ⁽¹¹⁾, ⁽¹²⁾ and contain them as special cases. Comparison of theoretical computations with the temperature dependence exhibited by Robert's $\alpha(\text{He} - \text{W})$ and $\alpha(\text{Ne} - \text{W})$ values gives satisfactory agreement. Brown ⁽¹⁰⁾ showed how Devonshire's formula may be used to obtain agreement with more recent experimental values of $\alpha(\text{He})$ and $\alpha(\text{Ne})$ on tungsten ⁽³⁶⁾, iron ⁽²⁸⁾, aluminum ⁽²⁹⁾ and platinum ⁽¹⁰⁾. However, in no case can α be calculated a priori from theory since agreement with experimental data is obtained only after judiciously adjusting several constants in the final formulas.

Devonshire also obtained the result that α is proportional to $1/\theta^3$ where θ is the characteristic temperature of the solid. Brown⁽¹⁰⁾ showed that upon making assumptions regarding the potential field which are necessary to achieve agreement between the Devonshire theory and experiment it is found that α is more nearly proportional to $1/M\theta^3$ where M is the molecular weight of the solid. Brown also observed that Devonshire did not consider the difference that can exist between the attractive and repulsive parts of the Morse potential function. Devonshire considered both parts to vary with the motion of the solid atom whereas, as pointed out by Jackson⁽⁶⁰⁾, the attractive part, which particularly at large distances depends on the average properties of a considerable volume of the solid in the neighborhood of the atom struck, should be stationary. Accordingly, Brown showed how Devonshire's treatment can be modified so as to disengage the attractive term in the Morse function from the oscillating solid atom.

Devonshire examined the effect on α of using a one-dimensional model and surmised that the result is an α value which is too large by a small amount.

The theory which has been described applies only to metallic surfaces which are reasonably free of adsorbed gases. Hence, it is only applicable to interactions between a metal surface and a gas which does not adsorb on that surface. Michels⁽⁶³⁾ attempted to relate α on a clean surface to α on a contaminated surface. However, to date, there is no known quantitative functional relation between α and the fraction of the surface which is covered, a relation which may be nonlinear.

We have thus far, in the discussion, failed to note that the accommodation coefficient for internal energy γ_i may be different than that for translational

energy α_t , and assumed with Knudsen⁽⁹⁾ that α_t and α_i have a common value α . According to Knudsen the effect of internal accommodation can be taken into account by the relation:

$$\alpha_t + \frac{3}{4} f \alpha_i = \frac{W_g}{\left[P / \sqrt{2 \pi M R T_g} \right] 2 R (T_s - T_w)} \quad (24)$$

where the r.h.s. is obtained from Equations (9) and (12) and the factor f depends on the molar heat capacities C_p and C_v at constant pressure and volume, respectively, and is given by:

$$f = \frac{5/3 - C_p/C_v}{C_p/C_v - 1} \quad (25)$$

When $\alpha_t = \alpha_i$, then the expression

$$\alpha = \frac{W_g}{\sqrt{R/2 \pi M T_g} (C_v/R + 1/2) (T_s - T_w)} \quad (27)$$

is obtained which is identical with the formula for α that results from combining Equations (9) and (13).

Knudsen's assumption that $\alpha_t = \alpha_i = \alpha$ is supported by results of his own experimental observations; however, there is also some contradictory evidence: Rowley and Bonhoeffer⁽⁶⁴⁾ measured accommodation coefficients of hydrogen on platinum and compared the accommodation coefficient of normal hydrogen with that of para-hydrogen at temperatures where p - H₂ has only translational energy but n - H₂ still has rotational energy in its ortho component. Measurements resulted in $\alpha_t = 0.43$ and $\alpha_{rot} = 0.26$ at 140°K and $\alpha_t = 0.44$, $\alpha_{rot} = 0.18$ at 170°K. Others (65) - (68) and (69), (70), (n.v.) have questioned the assumption that $\alpha_t = \alpha_i$ and proposed various analytical and experimental methods for determining α for polyatomic gases.

Jackson and Howarth⁽⁷¹⁾ attempted to modify the collision theory, previously described, to include the effect of rotation of diatomic molecules. They considered only repulsive interactions and two limiting cases: In one the gas molecule is treated as an oscillator, in the other as a plane rotator. In the first case the energy exchange between the rotations of the diatomic molecule and the vibrations of the solid is negligible; in the second, assuming the same repulsive field for the solid, the effect of rotation is small for Hydrogen and larger for Oxygen.

Other theoretical work includes (72) - (75) (n. v.) and a review paper by Herzfeld⁽⁷⁵⁾.

The energy exchange between a gas and a solid which takes place when a gas particle becomes adsorbed on the surface first and re-evaporated at a later time has also been treated theoretically^{(77) - (79)}. The distinction between this type of an interaction and the type considered previously viz: an inelastic collision followed "immediately" by reflection, is not always well defined. The assumption sometimes made⁽⁷⁷⁾ that all impinging gas atoms are temporarily adsorbed has not been generally demonstrated, and may be questioned in the case of helium, for example, interacting with a clean metal surface. The fact that the accommodation coefficient of helium on a clean surface appears to be unaltered by considerable variation in ΔT at constant T_g (see above) suggests that at least for helium adsorption does not play a major role in the energy exchange process.

CONCLUDING REMARKS

Accommodation coefficient values which can be confidently applied to a solution of satellite-drag and heat-transfer (80) problems must be obtained from experiments with gas molecules whose velocities match those of satellites. To our knowledge, the problem of generating in the laboratory a nearly mono-energetic beam of molecules in the range 1 - 10 eV with adequate flux has not yet been solved. Experimental facilities such as shock and arc tunnels which may produce molecular flows of nearly adequate velocities are not readily adaptable to α measurements. For these measurements the transient flow obtained in a shock tunnel is extremely inconvenient, while the composition and energy distribution of the gas obtained in an arc tunnel is not known with sufficient accuracy. With both facilities the problem of characterizing the composition of the surface is formidable. One may question the need for control of surface composition in experiments designed for satellite applications. However, the composition of a satellite surface in orbit, and hence the accommodation coefficient, will most probably differ appreciably from that of an untreated surface of the same material exposed to a laboratory vacuum of, say only, 10^{-7} mm of Hg. Furthermore, in orbit, satellite surface composition may change with changing surface temperature and ambient gas pressure, resulting in corresponding changes in α . Thus it may well be necessary to control in the laboratory, the composition of the surface in order to obtain useful data for satellite applications. Such control will certainly be necessary if the data are to be used to test theory.

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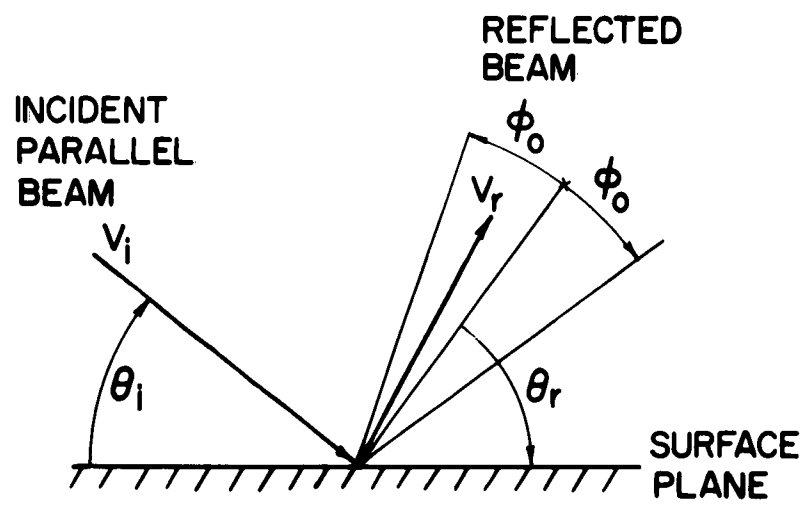


FIGURE 1

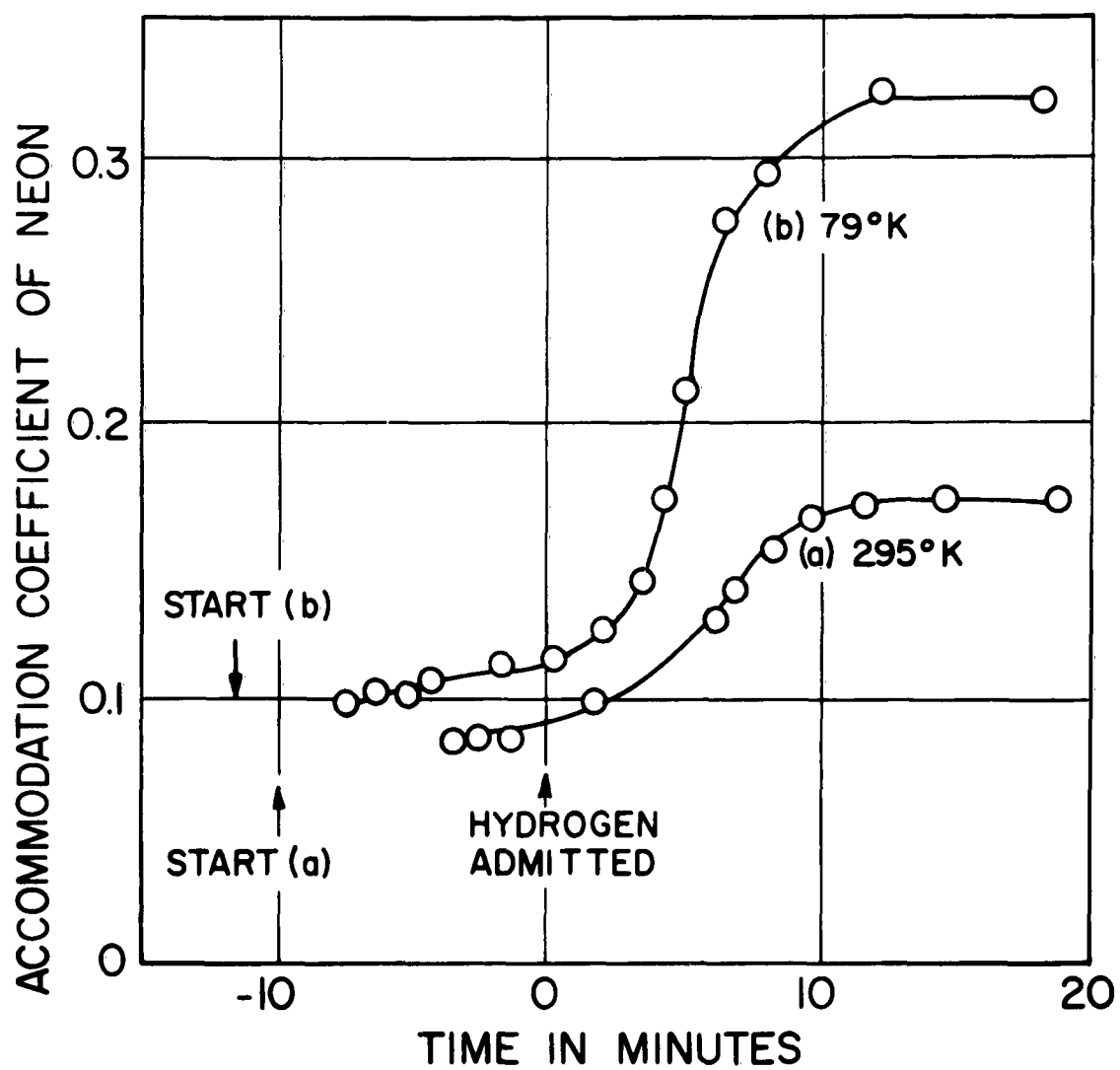


FIGURE 2

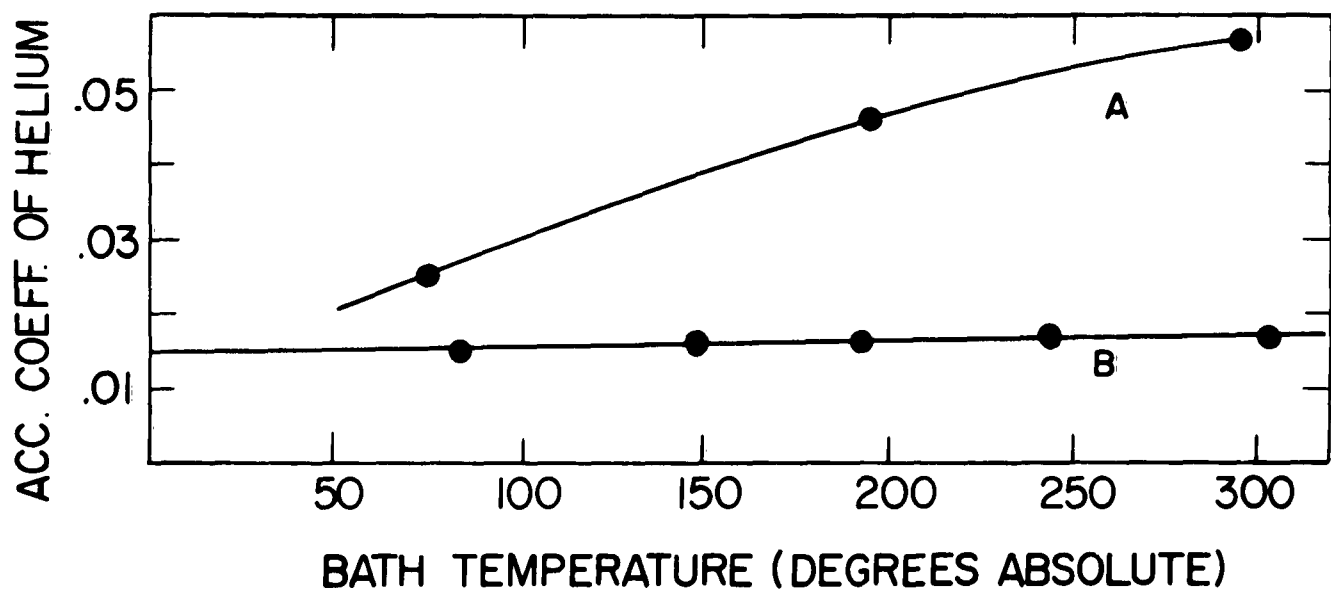


FIGURE 3

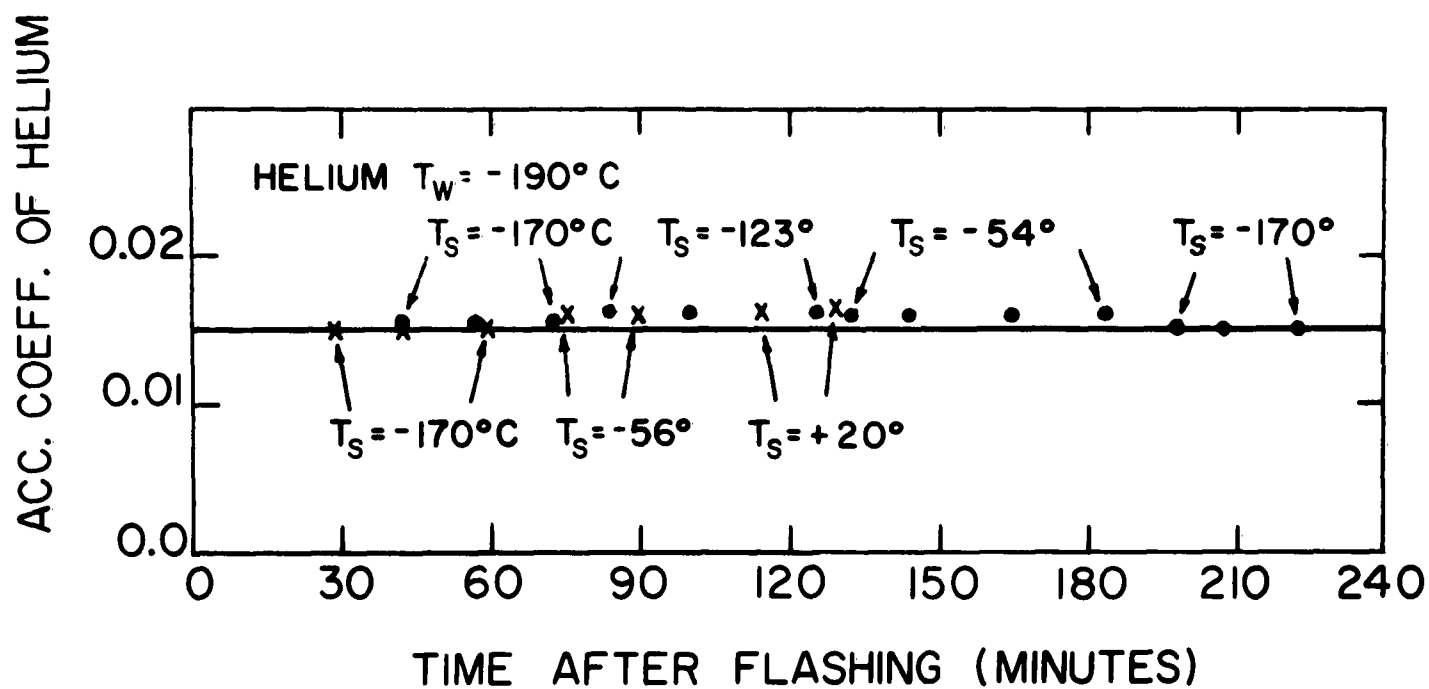


FIGURE 4

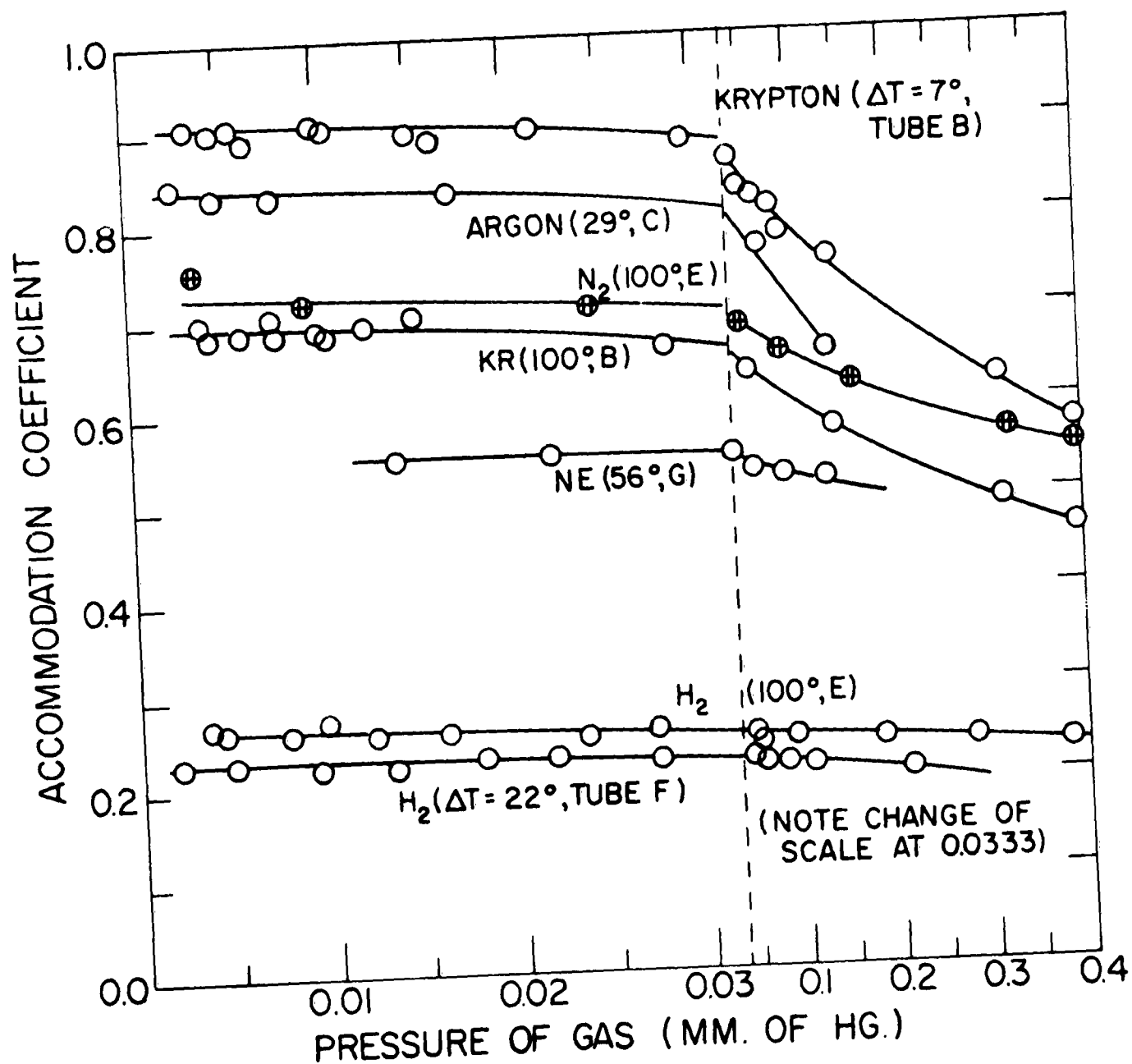


FIGURE 5

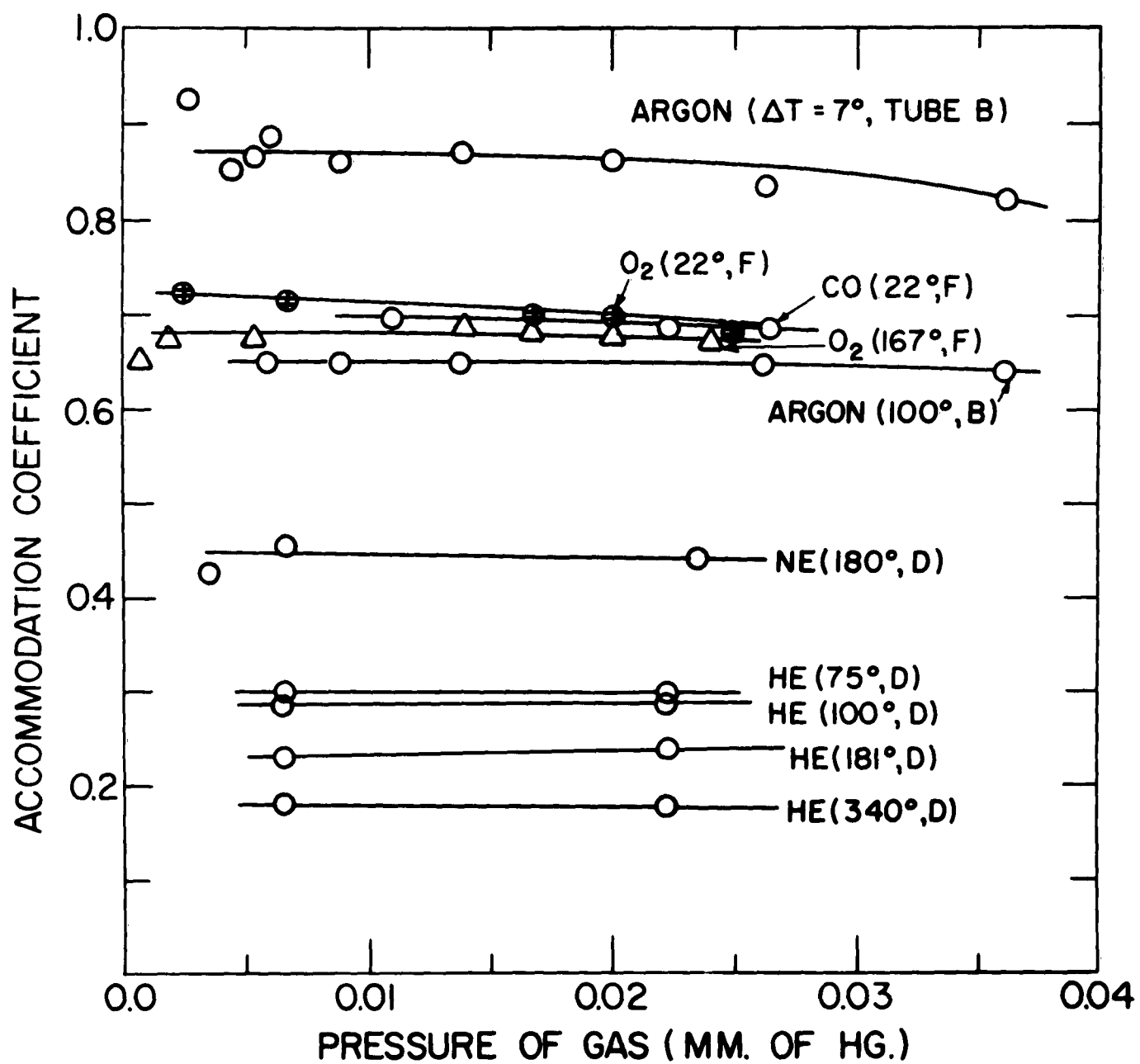


FIGURE 6

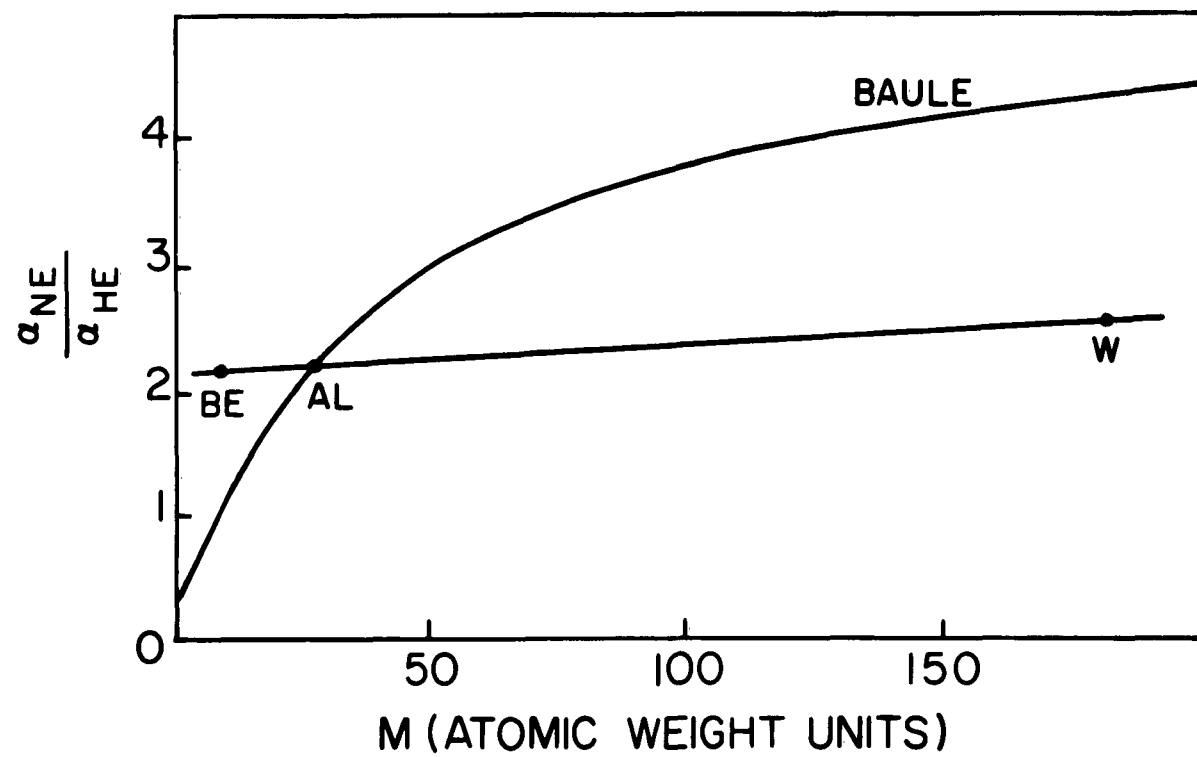


FIGURE 7

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