The Accommodation Coefficient of Helium on Platinum*

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The accommodation coefficient of helium on platinum has been measured at 77, 193, 273, and 373°K; and the values obtained at these temperatures for a clean platinum surface are 0.090, 0.043, 0.071, and 0.072 (±0.004), respectively. When the platinum is allowed to remain in contact with the helium for twenty-four hours or more, the accommodation coefficient values increase to 0.43, 0.071, 0.170, and 0.170 (in the same temperature order). Little adsorption occurs at 193°K, but strong van der Waals adsorption appears at 77°K and activated adsorption at the higher temperatures.

THE accommodation coefficient a of a gas striking a solid surface is defined by the following equation:

$$a=Q'/Q,$$

where Q' is the actual average energy exchange and Q is the energy exchange that would occur if the gas molecules, on the average, attained on collision the temperature of the solid surface. Since the accommodation coefficient is not independent of temperature, closely approaching solid and gas temperatures are understood.

The differential equation for the temperature distribution along a wire carrying a current and losing heat to its surroundings by radiation, conduction through the ends of the wire, and conduction to gas molecules impinging on its surface is:

$$d^2t/dx^2=At-B,^{1,2} \quad (1)$$

where

$$A=(1/K\pi r^2L)[8\pi e\sigma rT^3L+2(2\pi)^{\frac{1}{2}}aprL(R/MT)^{\frac{1}{2}}-I^2R_0cL] \quad (2)$$

and

$$B=I^2R_0/K\pi r^2L \quad (3)$$

are constants. The quantities involved are defined as follows:

I—current passing through wire,
R_0—resistance of wire at bath temperature,
e—emissivity of Pt at bath temperature,
K—thermal conductivity of Pt at bath temperature,
σ—Stefan-Boltzmann constant—5.722×10^{-12} watt cm^{-2} deg.$^{-4}$,
R—gas constant—8.314 joules °C^{-1},
c—temperature coefficient of resistivity,
r—radius of wire,
L—length of wire,
T—temperature of surrounding bath,
M—molecular weight of gas,
p—pressure of gas,
a—accommodation coefficient.

The solution of Eq. (1) for $A>0$ is:

$$t=\frac{B/A}{e^{\sqrt{A}L}-e^{-\sqrt{A}L}}\times[-(1-e^{\sqrt{A}L})e^{\sqrt{A}x}+(1-e^{\sqrt{A}L})e^{-\sqrt{A}x}]+B/A \quad (4)$$

and the average temperature of the wire is:

$$\bar{t}=B/A[f(A)-1], \quad (5)$$

where

$$f(A)=\frac{4-2(e^{\sqrt{A}L}+e^{-\sqrt{A}L})}{\sqrt{A}L(e^{\sqrt{A}L}-e^{-\sqrt{A}L})}. \quad (6)$$

Upon equating the heat supplied to the wire to the heat losses from the wire, the following equation results:

$$\frac{f(A)}{1-c\bar{t}}=-1+\frac{8\pi e\sigma rT^3Lm}{R_0c}+\frac{2(2\pi)^{\frac{1}{2}}aprL(R/MT)^{\frac{1}{2}}m}{R_0c}, \quad (7)$$

where

$$m=(R-R_0)/Q=R_0c\bar{t}/Q \quad (8)$$

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[1] J. K. Roberts, Proc. Roy. Soc. **A135**, 192 (1932).
[2] B. Raines, Phys. Rev. **56**, 691 (1939).

is a constant for a given bath temperature T, provided the power input is not too great.

Following the method of Cox,[3] one observes that the right-hand side of Eq. (7) is independent of the temperature rise; and, therefore, for zero power input,

$$f(A_0) = -1 + 8\pi e\sigma r T^3 L m/R_0 c + 2(2\pi)^{\frac{1}{2}} a p r L (R/MT)^{\frac{1}{2}} m/R_0 c. \quad (9)$$

Also, for zero power input, Eq. (2) for A becomes

$$A_0 = \frac{8\pi e\sigma r T^3 L - (2\pi)^{\frac{1}{2}} 2 a p r L (R/MT)^{\frac{1}{2}}}{K\pi r^2 L}. \quad (10)$$

And it can be seen from Eq. (9) that

$$-f(A_0) = 1 - (m/R_0 c) K\pi r^2 L A_0, \quad (11)$$

which defines a series of straight lines depending on the parameter,

$$N = (m/R_0 c) K\pi r^2 L. \quad (12)$$

At any fixed bath temperature K and c are known and m and R_0 are determined from the experimental data. Hence N is determined. Then, from the graphical simultaneous solution of (6) and (11), A_0 can be determined. When applied to a run in vacuum ($p < 1\times10^{-6}$ mm Hg) the second term in Eq. (10) falls out, and one can solve directly for the emissivity e. For a run in the presence of gas ($1\times10^{-3} < p < 1\times10^{-2}$ mm Hg) a can be evaluated from A_0, once the emissivity is determined by a run in vacuum at the same bath temperature. This method of calculating at zero power input has increased the precision and materially reduced the work of determining the accommodation coefficient from the experimental data.

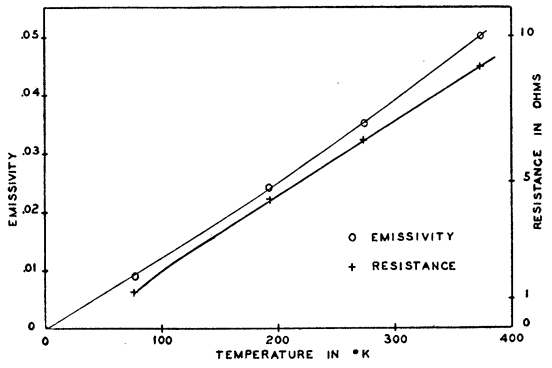

FIG. 1. Emissivity and resistance of platinum filament *vs.* temperature.

EXPERIMENTAL PROCEDURE

The vacuum system was a standard gas circulating system similar to those used by other workers in the field with the exception that all stopcocks directly in the path of the helium were replaced by mercury cut-offs. This was done to prevent contamination of the gas by stopcock grease. The helium was purified by high voltage discharge in a misch metal bottle. Pressures in the experimental tube were measured by a McLeod gauge connecting directly to the tube through a necessary mercury trap. The pressures read were corrected for the difference in temperature between the tube and the McLeod gauge.[1,4] Stepwise variations of pressure in the experimental tube were obtained by use of a mercury control. This consisted of two concentric glass tubes, the outer one connected to a lift containing mercury, the inner one containing a series of small holes of leak dimensions growing larger toward the bottom.

The experimental tube was somewhat pot-bellied in shape, being $3\frac{1}{2}$ cm wide at its widest point slightly below the center. This was to allow sideward sag of the platinum wire when it was flashed. The platinum (obtained from Baker and Company and of 99.99 percent purity) was in the form of a filament (14.23 cm long at room temperature, 2.65×10^{-3} cm in radius) supported vertically by tungsten leads without the use of springs. Since the flashing temperature of platinum (about 1200°C) is low, springs were unnecessary; and considerably greater accuracy can be obtained by their elimination.

The potential drop across the tube and across a ten-ohm standard resistance in series with it was measured with a Leeds and Northrup Type K potentiometer. Readings were taken with the current flowing first in one and then in the reverse direction to eliminate errors due to thermal e.m.f.'s. From these readings the resistance of the tube and its power input were determined.

The temperature of the medium surrounding the platinum was set by the use of fixed tempera-

[3] M. Cox, Phys. Rev. **64**, 241 (1943).

[4] O. Reynolds, Phil. Trans. **170**, 727 (1879).

TABLE I. Data under vacuum conditions.

Temperature °K	77.4	193.2	273.2	373.1
Resistance R_0 ohms	1.2562	4.4172	6.4475	8.9620±0.0001
Resistivity ρ ohm cm $\times 10^{-6}$	1.95	6.85	10.0	13.9 ±0.1
Thermal conductivity K watts/cm °C	0.796	0.679	0.695	0.715 ±0.005
Temp. coeff. resistivity $c=1/R_0 dR/dT$ °C$^{-1}\times 10^{-3}$	23.1	5.70	3.90	2.81 ±0.01
Emissivity e	0.009	0.024	0.035	0.050 ±0.001

ture thermostating baths. Ice, solid carbon dioxide and acetone, liquid air, and boiling water were used.

VACUUM DATA

Initially the resistance of the wire at 0°C was 6.4780 ohms, and the emissivity was equal to 0.057 (a thermal conductivity of 0.695 watt/cm °C is assumed).[5] The platinum was flashed first at 1000°C, then at 1200°C. At intervals the tube was thermostated and readings of R_0, e, and a were taken. After 100 hours of flashing, the ratio m/R_0 had become constant within its uncertainty, but the resistance at 0°C continued to decrease slowly; and it did not reach stability until after a thousand hours of flashing had elapsed.

Once stability had been attained at 0°C, runs were made at other temperatures. Reference to the equations will show that at zero gas pressure both the emissivity and the thermal conductivity of platinum enter. A search of the literature indicated some confusion in the values of the thermal conductivity of platinum. The best values appeared to be those by Holm,[5] whose work was done on platinum of 99.95 percent purity, and whose results are given by:

$$K=0.699[1+2.83\times 10^{-4}(T-292.7)] \text{ watt/cm°K.}$$

This formula was determined for temperatures above 0°C, so that its use at −80°C without substantiating data is to be questioned. But use of the calculated value (0.679) at this temperature leads to a value of the emissivity which falls on a smooth curve between the higher temperature values and the known value of zero at 0°K. The emissivity-temperature relationship is shown in Fig. 1. At 77.4°K the radiation loss (which is proportional to T^3) has become so low that it can be neglected, and the thermal conductivity is the only unknown. Unfortunately there is a limiting value of N for very small A_0 where the two expressions of $-f(A_0)$ are tangent over a considerable range, and there is quite a lack of precision. This value of N equals $L^2/2$. It is necessary, therefore, to use slightly different methods of computation at this temperature. Two were tried—first, using a non-zero power input Q and the corresponding average temperature $\bar{t}$; second, expanding $-f(A_0)$ in terms of power series in A_0 and neglecting all powers of A_0 higher than the first. The two methods gave the same value of K.

Figure 1 also includes a graph of the variation of the resistance of the platinum wire with absolute temperature (over the range 200–400°K it is close to a straight line). The vacuum data are summarized in Table I.

GAS DATA

Workers[1,2,6] in the field have long ago discovered that the accommodation coefficient is a function of the surface of the metal. In order to have meaning a must be measured on the metal itself: That is, the surface must be free of adsorbed or combined films. A clean surface can be obtained by flashing the metal at high temperatures in vacuum. But, unfortunately, as soon as the metal is allowed to cool in the presence of a gas, the surface becomes contaminated. Whether the contamination is due to adsorption of the impinging molecules of the pure gas or to the adsorption of minute impurities from the gas, the effect is practically the same. The accommodation coefficient will increase in value as time elapses. It is necessary then to extend the data back to the time of zero contamination. Two methods have been used to obtain this. The first, initiated

[5] R. Holm and R. Stormer, Wiss. Veroff. a. d. Siemens-Konzern **9**, 2, 312 (1930).

[6] W. C. Michels, Phys. Rev. **40**, 472 (1932).

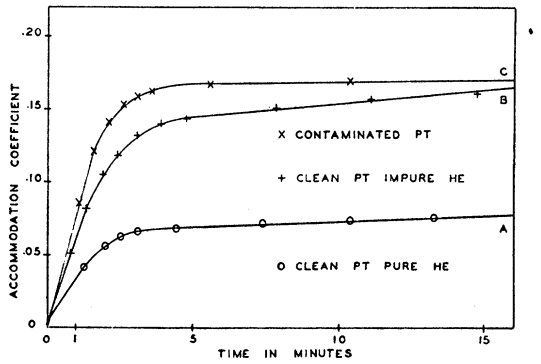

FIG. 2. Accommodation coefficient of helium on platinum *vs.* time after gas admission, 0°C, for clean and dirty platinum, pure and impure helium.

by Roberts,[1,7,8] consists of flashing the metal in vacuum, letting in the gas (metal still flashing) until equilibrium pressure is obtained, then suddenly cutting the flashing current off and taking readings of resistance against power input from that moment on. The second, used by Mann and Newall[9] and Raines,[2] consists of flashing the wire in vacuum until a clean surface is obtained, then letting in the gas and taking resistance-power readings from the time of entrance of the gas. Both methods were tried in this work under comparable conditions (hours aging of wire, gas purity, and pressure, etc.). It was noticed that at equal times after zero (10 min. or more) the first method invariably gave a higher accommodation coefficient than the second. On runs by the first method alone, a_0 increased whenever gas pressure was increased or the platinum was allowed to flash for longer times in the presence of the gas. There seemed to be only one reasonable explanation of this: namely, that residual impurities in the helium (despite the fact that the gas appeared pure viewed through a pocket spectroscope) were adsorbed upon the platinum when it was flashed in their presence, and, therefore, the first method gave a value of a_0 characteristic of an already contaminated surface. For this reason it was discarded, and the second method used throughout the remainder of the work.

Plotted in Fig. 2 are three curves representing the accommodation coefficient against time after the entrance of the gas for three runs at 0°C. Curve *A* was done with spectroscopically pure helium on platinum that had been flashed for many hours in vacuum before the run was taken and was presumably clean of adsorbed impurities. Curve *B* was taken with a clean wire but impure helium. Curve *C* was done in the following manner. The platinum was allowed to remain in the presence of the helium until a stable accommodation coefficient $a_\infty = 0.166$ was reached. The tube was then evacuated and a resistance-power measurement determined for $p < 1 \times 10^{-6}$ mm Hg. Then the gas was allowed to re-enter (no flashing had been done) and resistance-power measurements taken against time. Curve *C* shows the resulting accommodation coefficient. It is noticeable that it immediately rises from a zero value to the previously determined value of a_∞. But mere evacuation will not remove a film from a metal. Therefore the plotted values of a in the first few minutes after the gas entrance are not true measures of the accommodation coefficient. During this time the wire is cooling from its equilibrium temperature in vacuum to a lower temperature determined by ap, and an unsteady state exists. The equations for the determination of a assume a steady state (no time term), so that the apparent accommodation coefficient determined by them is not true until the temperature of the wire has ceased to lag behind the value determined by the energy losses.

Reference to curve *B* shows, however, that the fastest change in the accommodation coefficient is occurring in the early time intervals when the cooling lag is present. For the above reason it was decided to use logarithmic extrapolation of the accommodation coefficient to zero time, following the procedure suggested by Michels.[10] That this extrapolation is not always too good is only to be

TABLE II. Accommodation coefficient of He on Pt at zero time (a_0), some twenty minutes later (a_{eq}), and after twenty-four hours (a_∞).

Temp. °K	a_0	a_{eq}	a_∞
77.4	0.090	0.42	0.43
193.2	0.043	0.045	0.071
273.2	0.071	0.080–0.113	0.170
373.1	0.072±0.004	0.110	0.170

[7] J. K. Roberts, Proc. Roy. Soc. **A129**, 146 (1930).
[8] J. K. Roberts, Proc. Roy. Soc. **A142**, 518 (1933).
[9] W. B. Mann and W. C. Newall, Proc. Roy. Soc. **A158**, 397 (1937).
[10] W. C. Michels, Phys. Rev. **52**, 1067 (1937).

expected. The presence of more than one impurity with different rates of film build-up is logical; an actual saturation effect (that is—entrance of the impurity within the body of the platinum) is possible.

The accommodation coefficient data are summarized in Table II for the four different bath temperatures used. By a_0 is meant the accommodation coefficient at zero time, and the values of it given in the table were obtained by logarithmic extrapolation except at 193.2°K where no adsorption occurred until many hours had passed. By a_{eq} is meant the value of the accommodation coefficient obtained some ten to twenty minutes after the entrance of the gas. At this time the value of the accommodation coefficient is changing very slowly. By a_∞ is meant the accommodation coefficient 24 hours or more after the gas has been let in. Figure 3 shows representative runs at each temperature for thirty minutes after gas admission. Although the curves have been shown extrapolated to zero time the values of accommodation coefficient obtained by such extrapolation mean little because of the cooling lag of the platinum present in the first few minutes, and the actual values of a_0 were obtained by linear logarithmic extrapolation.

There are some points of interest in the accommodation coefficient data obtained. The values of a_0 at 273°K and 373°K, i.e., 0.071 and 0.072, respectively, are in fair agreement with the classical value[10] of 0.078 determined from

$$4mM/(m+M)^2,$$

where m and M are the atomic weights of platinum and helium. The low value of a_∞ (0.170) at these temperatures indicates a tightly bound adsorbed film on the platinum and, therefore, activated adsorption of minute impurities present in the helium. At 77.4°K the high value of a_∞ (0.43) combined with the fact that the best straight line logarithmic extrapolation was found at this temperature strongly indicates van der Waals adsorption of helium.

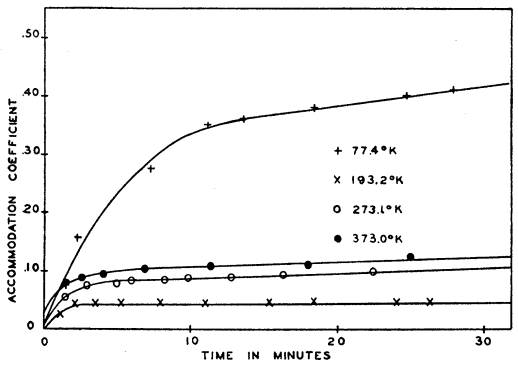

FIG. 3. Accommodation coefficient of helium on platinum *vs.* time after gas admission for various bath temperatures.

In Table III are presented values of the accommodation coefficient of helium on several metals found by other authors. Comparison of the values of a determined in this work with those determined by Mann[11] (He on Pt) are difficult because at no time in the latter's work did the filament temperatures run below 100°C. In the one comparable case (both bath and filament temperatures at 100°C) agreement is obtained for a_0 (0.07 against 0.072). There seems to be little correlation between the present work and the other two sets of data (He on Ni[2] and W[1]) shown in Table III. In the case of the nickel data which were determined by experimental means very similar to this work no attempt was made to allow for a possible lag in cooling of the nickel when the gas was admitted. None of the three sets of data presented in Table III shows the characteristics of the helium on platinum accommodation coefficient data discovered in this work, i.e., a region of strong van der Waals adsorption at very low temperatures, followed by a region of no adsorption and finally an extended region of activated adsorption as the temperature is increased.

TABLE III. Accommodation coefficients of He on Ni, W, and Pt.

Temp. °K	Accommodation coefficients found by other workers					
	He on Ni[2]		He on W[a]		He on Pt[b]	
	a_0	a_∞	a_0	a_∞	a_0	a_∞
77.4	0.048	0.410	0.025	—	0.04*	—
195	0.060	0.423	0.046	—	—	—
273	0.071	0.360	0.057	0.19 (295°K)	0.03†	—
373	0.077	0.343	—	—	0.07	0.25

[a] See reference 1.
[b] See reference 11.
* Bath temperature 80°K, filament temperatures 100°C and up.
† Bath at room temperature, filament between 100°C and 1000°C.

[11] W. B. Mann, Proc. Roy. Soc. **A146**, 776 (1934).