AIP The Journal of Chemical Physics

Accommodation Coefficients on Gas Covered Platinum

I. Amdur, Margaret McCormack Jones, and H. Pearlman

Citation: The Journal of Chemical Physics **12**, 159 (1944); doi: 10.1063/1.1723929
View online: http://dx.doi.org/10.1063/1.1723929
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/12/5?ver=pdfcov
Published by the AIP Publishing

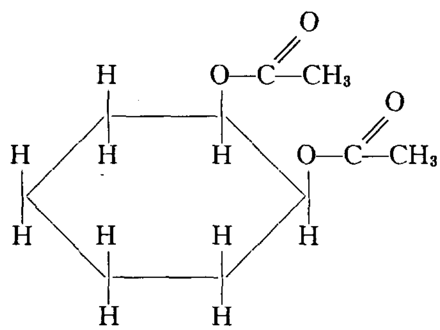
ETHYL *p*-TOLUENESULFONATE

Ethyl *p*-toluenesulfonate,

$$CH_3—C_6H_4—SO_2OC_2H_5.$$

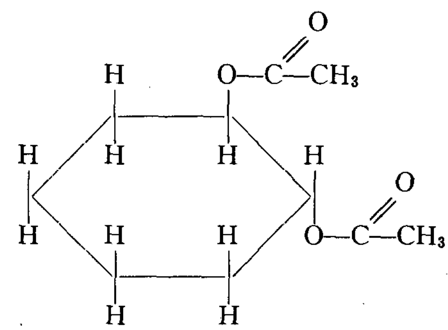
Prepared by Charles Jones by the action of an ether solution of *p*-toluenesulfonylchloride on ethyl alcohol in the presence of sodium hydroxide. B.p. 143° at 2–3 mm. The spectrum is given in Table III.

cis- AND *trans*-1,2-DIACETOXYCYCLOHEXANE



cis-1,2-Diacetoxycyclohexane.

Synthesized by acetylation of the corresponding *cis*-glycol by Howard Hess, who also obtained the spectrum of the compound. B.p. 117.8–118.0° at 12 mm, n_D^{25} 1.4475.



trans-1,2-Diacetoxycyclohexane.

Synthesized by the action of silver acetate on the *trans*-bromohydrin by Robert Buckles, who also obtained the spectrum of this compound. B.p. 119.8–120.0° at 12 mm, n_D^{25} 1.4458.

ACKNOWLEDGMENT

The authors wish to acknowledge the work of the several students who prepared and obtained the spectra of a number of the compounds.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 12, NUMBER 5 MAY, 1944

Accommodation Coefficients on Gas Covered Platinum *

I. AMDUR, MARGARET MCCORMACK JONES, AND H. PEARLMAN
Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received March 1, 1944)

Accommodation coefficients on a platinum wire have been computed for five monatomic and five diatomic gases from Pirani gauge measurements at room temperature, 18.9° to 30.5°C. Through careful control of experimental conditions it was possible to apply exact theoretical relations for the effects of radiation, wire conduction, and free molecule conduction upon the temperature distribution along the gauge wire. For each of the gases the accommodation coefficient increases with pressure up to about 0.1 mm and then remains constant throughout the pressure range in which complete free molecule conduction exists, indicating the absence of complete gas saturation of the wire surface at the lower pressures. There is no detectable temperature coefficient in the small interval in which measurements were made. At room temperature the mean accommodation coefficients on a completely gas covered platinum wire are: helium, 0.403 ± 0.001; neon, 0.700 ± 0.002; argon, 0.847 ± 0.002; krypton, 0.844 ± 0.002; xenon, 0.858 ± 0.002; hydrogen, 0.312 ± 0.001; deuterium, 0.393 ± 0.001; nitrogen, 0.769 ± 0.002; carbon monoxide, 0.772 ± 0.002; oxygen, 0.782 ± 0.002.

ACCURATE values of accommodation coefficients of gases on solids are required for the estimation of energy transport by gases at low pressures. Values for gas covered platinum wire are of particular interest since a heated platinum wire is used frequently as an energy

* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 506.

source in pressure measuring devices such as Pirani gauges. Since the physical constants of platinum are very well known, the response of such a gauge as a function of pressure for a given gas can be predicted with accuracy if reliable values are available for the accommodation coefficient.

Thomas and Olmer[1] have recently published values of accommodation coefficients on gas covered platinum. Although they appear to have analyzed correctly the heat flow problem, their values are not considered characteristic of completely gas covered platinum by the present authors because of the low pressures (less than 0.05 mm) used in their experiments. The present results show that for many of the gases they studied saturation of the platinum surface is not attained at pressures less than about 0.1 mm and that at lower pressures the accommodation coefficients increase with pressure. The excellent summaries and discussions of the available

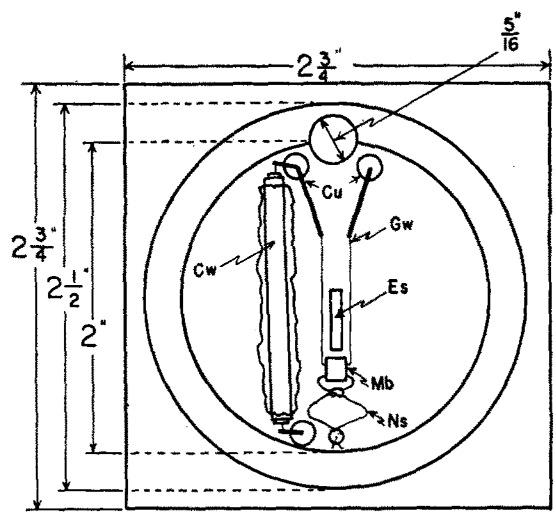


FIG. 1. Details of conductivity gauge.

information on accommodation coefficients on gas covered platinum given by Thomas and Olmer and by Kennard[2] indicate that reliable experimental values are, in most cases, still to be obtained. The authors feel that it is desirable to present their values, obtained before publication of the paper by Thomas and Olmer, since they believe that the careful control of experimental conditions to permit the analysis of results according to rigorous kinetic theory and heat flow theory and the numerous measurements over a sufficiently wide pressure range to insure surface saturation have resulted in accommodation coefficients of high accuracy.

EXPERIMENTAL

Measurements were made at room temperature on five monatomic and five diatomic gases; helium, neon, argon, krypton, xenon, hydrogen, deuterium, nitrogen, carbon monoxide, and oxygen. Accommodation coefficients were computed from the quantity of heat required to raise by about 2° the average temperature of a bright platinum wire surrounded by gas confined between two parallel brass plates. The conductivity gauge was originally designed to contain gases, at pressures measured by the self-contained compensated Pirani gauge, for the scattering of molecular beams. It was, in effect, a short circular brass cylinder, 2 inches in diameter and about $\frac{1}{8}$ inch high, made of two close fitting parts which were soldered together to make a chamber whose only openings were a $\frac{5}{16}$-inch port for evacuation or admission of gas, a 0.020-inch beam entrance hole, and a narrow exit slot. Figure 1 is a diagram of the gauge with the top cover removed. The gauge wire G_w about 4.5 cm long, is bent into a U around the exit slot E_s and lies in a plane midway between the parallel confining surfaces of the upper and lower sections. Jaws on the bottom face of the lower section close over the exit slot to define a slit 0.0003 inch wide. The ends of the gauge wire are soldered to copper rods *Cu*, which are soldered through Kovar metal sleeves sealed into insulating beads of Corning AJ705 glass. The beads are sealed into other concentric Kovar sleeves which are soldered through the brass case of the unit. At the bend of the U the wire passes through a hole in a supporting block of Mycalex *Mb*, which is anchored to a nickel wire 0.008 inch in diameter bent in the form of a bow spring *Ns*. The spring which exerts light tension on the gauge wire is fastened to the brass case with a small watch screw.

A wire having as closely as possible the resistance of the gauge wire was cut from the same

[1] L. B. Thomas and F. Olmer, J. Am. Chem. Soc. **65**, 1036 (1943).

[2] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), pp. 320–323.

stock as the gauge wire. It was placed between two strips of mica about 0.0003 inch thick by $\frac{1}{16}$ inch wide and drawn through a thin walled platinum tube that had been previously rolled to an oval cross section. The assembly C_w was then flattened and well soldered to the case. This second wire forms an arm of the Wheatstone bridge and serves to compensate for changes in temperature of the brass case. The other two arms of the bridge are wire wound manganin resistors imbedded in ceresin and enclosed in a vacuum tight brass case which is fastened to the main unit. At 26°C the arms of the bridge have the following resistances; gauge wire R_g, 36.22_0 ohms; compensator R_c, 37.62_4 ohms; manganin resistor R_1, 24.60_1 ohms; manganin resistor R_2, 25.37_3 ohms. At a given case temperature a comparatively small current, depending upon the gas pressure, will raise the temperature of the gauge wire and have no effect upon the temperature of the other arms. When this temperature rise is about 2° the bridge will be in balance, that is, $R_g/R_c = R_1/R_2$.

The complete gauge assembly was placed in a bell jar containing the desired gas at an accurately known low pressure obtained by expansion from a smaller volume at a higher accurately measurable pressure. Figure 2 is a schematic diagram of the system used in the above manner. After evacuating the entire system, a given pressure is obtained in the bell jar by letting gas into F to the desired initial high pressure read on the manometer with a cathetometer. In the experiments using helium, argon, nitrogen, and hydrogen which were compressed in metal cylinders, the gas passed through an oil bubbler and a liquid nitrogen trap before expansion into F. After the initial pressure in F has been read, the manometer is shut off and the desired final pressure in N (and accompanying volumes) is obtained by a series of expansions into E and N from F. All pertinent volumes were carefully determined by appropriate calibrations. Since all parts of the system were not at the same temperature, thermometers were lashed to E and F and suspended inside N.

For a given pressure in N, the current required to balance the bridge is read on a sensitive multi-range milliameter ($\frac{1}{4}$ percent full scale accuracy) in series with the bridge. This reading depends primarily upon the pressure in N and to a slight extent upon the temperature of the bridge network. Since the temperature-resistance characteristics of the network are known, it is possible to correct for this temperature effect so that the meter readings become single-valued functions of the pressure for a given gas.

Care was taken to insure that the gases used in the experiments were of very high purity. Helium, originally 96 percent, was passed at 2000 pounds per square inch pressure over

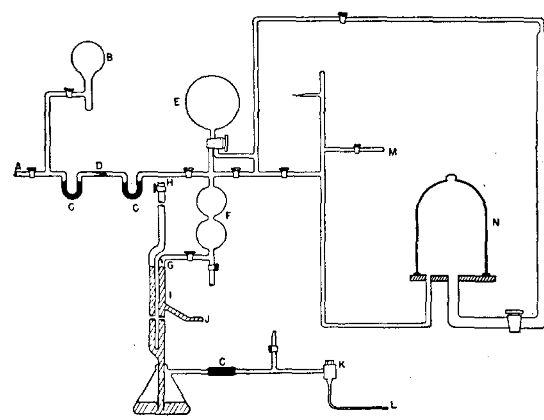


FIG. 2. System for producing and measuring gas pressures. A, Connection to gas feed-in system (for helium, argon, hydrogen, nitrogen, and oxygen). B, Gas supply (for neon, krypton, xenon, deuterium, and carbon monoxide). C, Glass wool filter. D, Capillary throttle. E, Standard volume (2199 ml). F, Standard volume (429.9 ml). G, Manometer dead space (2.15 ml). H, Connection to vacuum system. I, Manometer. J, Connection to mercury injector. K, Metal stopcock. L, Connection to nitrogen tank. M, Connection to trap and McLeod gauge (for rough check of pressure). N, Bell jar (14,800 ml including connecting tubing). O, Connection to trap and vacuum system.

activated charcoal at liquid nitrogen temperature. It is estimated that this produced a final product of at least 99.9 percent purity. The argon, originally 99.9 percent, was passed at 1700 pounds per square inch over activated charcoal at liquid nitrogen temperature. Neon, krypton, and xenon were obtained 99.9 percent pure in Pyrex bulbs from Linde Air Products Company and used without further purification.

Nitrogen, oxygen, and hydrogen were obtained in cylinders from the Puritan Compressed Gas Company, Inc. The nitrogen was 99.5 percent and was passed at atmospheric pressure over activated charcoal cooled with acetone-dry ice mixture. The oxygen and hydrogen were 99.9 percent and were used without further purification. Deuterium was prepared by treating deuterium oxide, 99.9 percent, with sodium. Carbon monoxide was made by the sulfuric acid-formic acid method and passed through a liquid nitrogen cooled trap into a one-liter storage bulb. It is felt that this procedure should produce gas of at least 99.9 percent purity.

FUNDAMENTAL RELATIONS

The equation for the distribution of temperature along a current bearing wire whose ends are maintained at a fixed temperature has been developed by Roberts[3] and extended by Raines[4] to include a correction for the increase in resistance due to heating of the wire. When the temperature difference Δt between any point on the wire and the surroundings is small so that $4T_0{}^3\Delta t$ is a sufficiently accurate approximation to $T^4-T_0{}^4$ (where T is the absolute temperature of a point on the wire and T_0 that of the surroundings or wire ends), the differential equation which equates the rate at which energy is removed from unit length of the wire by radiation, metallic and gaseous conduction to the rate of energy input by electric current is

$$\frac{d^2(\Delta t)}{dx^2}-A(\Delta t)+B=0,$$

for which the solution is:

$$\Delta t=\frac{B}{A}\left[1+\frac{\sinh A^{\frac{1}{2}}(x-l)-\sinh A^{\frac{1}{2}}x}{\sinh A^{\frac{1}{2}}l}\right]. \quad (1)$$

A and B have the values:

$$A=\frac{8\epsilon\sigma(T_0)^3}{rK_{t_0}}+\frac{2}{rK_{t_0}}\left[\frac{1}{2\pi MRT'}\right]^{\frac{1}{2}} \times(C_v+\tfrac{1}{2}R)aP'-\alpha B, \quad (2)$$

$$B=\frac{I^2R_{t_0}}{\pi r^2 lK_{t_0}}, \quad (3)$$

where I = heating current in wire, r = wire radius, K_{t_0} = thermal conductivity of the wire at the temperature of the ends, ϵ = total emissivity of bright platinum at room temperature, σ = Stefan-Boltzmann constant, M = molecular weight of gas, R = gas constant per mole, Δt = temperature excess above temperature of the ends, R_{t_0} = resistance of 1 cm of wire at temperature of the ends, α = temperature coefficient of resistance of the wire, C_v = molar heat capacity at constant volume, P' = average gas pressure, T' = average absolute temperature of gas, a = accommodation coefficient, t_0 = centrigrade temperature of the ends or surroundings, T_0 = absolute temperature of the ends or surroundings, and l = length of wire of resistance R_{t_0} at temperature of the ends.

The first term in Eq. (2) arises from heat lost through radiation and the last term from heat gained due to the increase in resistance of the wire with increasing temperature. The second term takes account of the heat lost by free molecule gas conduction. Kennard[5] considers this term in detail and shows that the average absolute temperature of the gas T' is a function of the average absolute temperature of the wire $\bar{T}$, of the absolute temperature of the surroundings T_0 and the accommodation coefficients on the wire and case. Since the accommodation coefficient of the gas on the case is always unity because of the infinite radius of curvature of the case relative to the wire, it is only necessary to take into account the accommodation coefficient of the gas on the wire. Because $\bar{T}$ exceeds T_0 by only 2 degrees, T' may in all cases be taken as the arithmetic mean of $\bar{T}$ and T_0 with a maximum possible error (for the case of the accommodation coefficient of the gas on the wire equal to zero) of 0.3 percent. The average gas pressure in the gauge P' is given by $P_0(T'/T_0)^{\frac{1}{2}}$ where P_0 is the actual pressure in the surroundings at T_0.

From the known characteristics of the Wheatstone network the resistance of the gauge wire at the balance point may be computed. This resistance is a function only of the mean temperature of the wire so that it is the mean temperature excess $\overline{\Delta t}$ which is of interest rather than the temperature excess Δt of a given point on the wire. Substitution of Eq. (1) into the relation

$$\overline{\Delta t}=\frac{1}{l}\int_0^l \Delta t dx$$

gives the following relation for the mean temperature excess of the gauge wire

$$\overline{\Delta t}=\frac{B}{A}\left[1+\frac{2(1-\cosh A^{\frac{1}{2}}l)}{A^{\frac{1}{2}}l\sinh A^{\frac{1}{2}}l}\right] =\frac{B}{A}\left[1-\frac{2\tanh\frac{1}{2}A^{\frac{1}{2}}l}{A^{\frac{1}{2}}l}\right]. \quad (4)$$

[3] J. K. Roberts, Proc. Roy. Soc. **A135**, 192 (1932).
[4] B. Raines, Phys. Rev. **56**, 691 (1939).
[5] E. H. Kennard, reference 2, pp. 311–318.

The accommodation coefficient a is determined from experimental quantities in the following manner. The mean temperature excess at 26°, $\overline{\Delta t}_{26}$, is known from the characteristics of the Wheatstone network. In terms of this standard value the mean temperature excess at any other temperature, Δt_{t_0}, is given by

$$\overline{\Delta t}_{t_0}=\overline{\Delta t}_{26}[1+\alpha(t_0-26)]. \qquad (5)$$

This very small variation of the mean temperature excess with temperature is due to the inclusion of the compensator in the bridge. The current through the gauge wire I may be computed from the measured total bridge current and the resistance values of the bridge arms at balance. Thus at a given case temperature and gas pressure $\overline{\Delta t}_{t_0}$ and B are known so that A may be obtained by graphical solution of Eq. (4). Substitution of this A value into Eq. (2) gives a value for a since all other quantities are known.

PHYSICAL CONSTANTS OF THE GAUGE WIRE

The physical constants of the gauge wire must be accurately known if reliable values for the accommodation coefficients are to be obtained. In the present investigation these constants were obtained in the following manner.

A. Length, l

From the same piece of platinum wire of which about 4.5 cm were used in the gauge, about 5 cm were placed between rigid supports and the exact length measured with a cathetometer. The resistance per unit length was determined and from the resistance of the gauge wire the length of the gauge wire was found to be 4.57 cm. This is not the effective length of the gauge, however, since 3 mm of the wire pass through the Mycalex support block. From calculation of the wire conduction loss at zero pressure and estimation of the heat loss through the Mycalex block and supporting wires, it was found that the block was heat stationed at the temperature of the brass case. Thus 3 mm of the wire are not heated by the bridge current and the gauge must be regarded as two separate wires each 2.13_5 cm long whose ends are at the temperature of the case. In Eqs. (1) and (4) the length of the wire l refers to this value. In Eq. (3) it is only necessary that mutually consistent values of R_{t_0} and l be used.

The heat stationing effect of the Mycalex block must also be taken into consideration in evaluating the mean temperature excess of the gauge wire at the bridge balance point. At the reference temperature 26°C, the relation is:

$$\overline{\Delta t}_{26}=\frac{R_1R_c-R_2R_g}{R_2R_gx\alpha}, \qquad (6)$$

where x is the fraction of the length of the gauge wire outside the Mycalex block. Insertion of the proper numerical values in Eq. (6) yields 2.114° for $\overline{\Delta t}_{26}$.

B. Temperature Coefficient of Resistance, α

The temperature coefficient of resistance of the gauge wire was found by measuring the resistance at 54.25°C and at 0°C. The average coefficient in this range was found to be 3.63×10^{-3} deg.$^{-1}$.

C. Resistivity, ρ

Matthiessen's rule[6] states that in working a pure platinum wire the resistivity ρ and the coefficient of resistance α may change in value at a given temperature, but only in such manner that the product of the two is constant. By using the values of ρ at 0°C and of α in the range 0°–54.25°C as given for pure platinum in the *International Critical Tables*,[7] ρ at 0°C for the platinum in the gauge wire was found to be 10.694×10^{-6} ohm-cm. Combining this value with the measured α, 3.63×10^{-3}, ρ_{26} for the gauge wire is found to be 11.703×10^{-6} ohm-cm.

D. Radius, r

The radius of the gauge wire as determined from the relation

$$r=\left[\frac{\rho_{26}l}{\pi R_{26}}\right]^{\frac{1}{2}}$$

is 6.86×10^{-4} cm.

[6] A. Matthiessen and C. Vogt, Pogg. Ann. **122**, 19 (1864).
[7] *International Critical Tables* (McGraw-Hill Book Company, Inc., 1929), Vol. 6, p. 136 (second set of values).

TABLE I.

Gas	t_0 (°C)	I_B (ma)	P (mm)	a
He	25.2	2.205	0.009639	(0.258)
	19.2	2.199	0.01011	(0.296)
	18.9	2.787	0.04097	(0.386)
	22.0	2.959	0.05250	(0.376)
	21.4	3.110	0.06076	(0.392)
	21.8	3.335	0.07714	(0.391)
	29.3	3.645	0.09940	(0.385)
	19.1	3.780	0.1127	0.398
	21.6	4.165	0.1450	0.400
	22.0	4.460	0.1740	0.398
	21.7	4.735	0.1995	0.406
	29.0	4.930	0.2210	0.394
	19.0	5.155	0.2461	0.411
	21.2	5.275	0.2596	0.408
	22.9	5.470	0.2854	0.403
	21.7	5.750	0.3223	0.404
	25.2	5.905	0.3417	0.400
	19.1	6.010	0.3583	0.406
				Mean 0.403
				±0.001
Ne	25.3	2.195	0.01104	(0.466)
	25.5	2.233	0.01374	(0.487)
	27.8	2.740	0.04714	(0.642)
	26.9	2.905	0.06002	(0.659)
	27.4	3.400	0.1018	0.685
	24.2	4.055	0.1709	0.700
	25.1	4.570	0.2322	0.705
	24.9	4.990	0.2900	0.706
	27.8	5.500	0.3669	0.700
	25.6	5.655	0.3940	0.703
	27.2	6.050	0.4671	(0.691)
				Mean 0.700
				±0.002
A	25.6	2.145	0.01095	(0.445)
	26.5	2.215	0.01312	(0.612)
	25.2	2.709	0.05125	(0.807)
	25.9	3.270	0.1045	0.833
	25.3	3.760	0.1589	0.851
	25.6	3.800	0.1643	0.847
	25.6	4.190	0.2157	0.848
	26.7	4.280	0.2252	0.856
	25.3	4.770	0.3015	0.853
	25.9	5.050	0.3497	0.845
	25.6	5.260	0.3883	0.842
				Mean 0.847
				±0.002
Kr	25.8	2.100	0.009823	(0.232)
	28.3	2.510	0.04863	(0.776)
	28.2	2.625	0.06158	(0.800)
	28.2	2.960	0.1040	0.826
	25.7	2.980	0.1077	0.842
	26.0	3.250	0.1451	0.850
	25.8	3.490	0.1818	0.857
	25.6	3.695	0.2173	0.855
	26.0	3.835	0.2451	0.843
	26.0	4.075	0.2914	0.841
	26.1	4.355	0.3484	0.841
	28.2	4.500	0.3764	0.840
	26.1	4.665	0.4165	0.840
	28.2	4.900	0.4766	(0.826)
				Mean 0.844
				±0.002
Xe	26.0	2.080	0.007116	(0.108)
	26.7	2.127	0.01127	(0.454)
	27.4	2.360	0.03784	(0.794)
	25.9	2.527	0.06307	(0.810)
	26.0	2.630	0.07540	(0.848)
	26.0	2.950	0.1250	0.865
	27.4	3.230	0.1725	0.869
	26.0	3.420	0.2111	0.866
	26.1	3.600	0.2524	0.849
	25.9	3.775	0.2891	0.856
	27.2	3.950	0.3352	0.835
	25.7	4.250	0.3986	0.864
				Mean 0.858
				±0.002
H_2	26.5	2.310	0.008717	(0.239)
	25.8	2.350	0.009725	(0.257)
	23.2	3.400	0.04916	(0.309)
	25.9	4.400	0.1013	0.311
	24.0	4.440	0.1027	0.316
	24.0	5.205	0.1536	0.316
	26.7	5.850	0.2039	0.312
	26.6	6.335	0.2479	0.309
	26.3	6.995	0.3111	0.309
	26.0	7.285	0.3434	0.308
				Mean 0.312
				±0.001
D_2	24.8	2.365	0.01162	(0.324)
	25.4	3.300	0.04888	(0.388)
	25.3	3.550	0.06222	(0.386)
	23.6	4.275	0.01041	0.395
	25.3	4.295	0.1056	0.392
	24.9	4.850	0.1439	0.394
	23.5	5.280	0.1767	0.398
	22.1	5.610	0.2048	0.399
	23.3	5.675	0.2112	0.396
	24.7	6.472	0.2903	0.389
	24.8	6.994	0.3470	0.389
	25.5	7.275	0.3804	0.387
	24.5	7.540	0.4148	(0.385)
				Mean 0.393
				±0.001
N_2	25.7	2.225	0.009121	(0.543)
	27.1	2.298	0.01146	(0.625)
	25.5	3.040	0.04950	(0.758)
	26.0	3.670	0.09147	0.765
	25.7	3.784	0.1008	0.761
	26.0	3.910	0.1106	0.761
	25.5	4.440	0.1524	0.784
	26.4	5.030	0.2107	0.776
	25.7	5.100	0.2181	0.775
	24.8	5.765	0.2973	0.767
	25.5	5.985	0.3255	0.763
				Mean 0.769
				±0.002
CO	28.4	2.240	0.008454	(0.586)
	30.0	3.150	0.05471	(0.756)
	28.6	3.700	0.09192	(0.768)
	29.2	4.100	0.1216	0.778
	28.5	4.725	0.1778	0.776
	29.2	5.030	0.2064	0.781
	30.0	5.410	0.2509	0.765
	28.7	5.840	0.3017	0.768
	28.4	6.070	0.3311	0.767
				Mean 0.772
				±0.002

TABLE I.—*Continued.*

Gas	t_0 (°C)	I_B (ma)	P (mm)	a
O_2	30.1	2.220	0.008557	(0.491)
	30.5	3.025	0.05029	(0.742)
	28.7	3.640	0.09046	0.787
	28.8	4.035	0.1226	0.782
	29.6	4.375	0.1520	0.784
	28.3	4.950	0.2080	0.792
	30.5	5.145	0.2306	0.779
	29.2	5.385	0.2579	0.782
	30.1	5.750	0.3054	0.770
	28.6	5.920	0.3259	0.777
				Mean 0.782 ±0.002

E. Thermal Conductivity, K

According to the Wiedemann-Franz relation the ratio of the thermal and electrical conductivities at a given temperature is the same for all pure metals. Therefore, from the values of the resistivity and thermal conductivity[8] of pure platinum and from ρ_0 for the gauge wire, the thermal conductivity K_0 at 0°C for the platinum in the gauge wire may be calculated directly. It has a value of 0.639 watt/cm-degree and varies with temperature according to the relation[8]

$$K_t = K_0[1+0.53\times10^{-3}t].$$

F. Total Emissivity, ε

The total emissivity of bright platinum increases slowly with temperature and at room temperature may be represented with sufficient accuracy from experimental values[9] by the relation

$$\epsilon_T = 0.0359[1+2.6\times10^{-3}(T-300)].$$

RESULTS

All experimental results and derived accommodation coefficients are given in Table I. I_B is the measured total bridge current from which the current through the gauge wire may be calculated. In calculating values for the accommodation coefficients from Eq. (3) the molar heat capacity at constant volume C_v was taken as $\frac{3}{2}R$ or 2.980 calories/mole-degree for each of the rare gases. For the diatomic gases C_v, computed from the molar heat capacities at constant pressure calculated from spectroscopic data,[10] had the following values: hydrogen, 4.909; deuterium, 4.990; nitrogen, 4.973; carbon monoxide, 4.977; oxygen, 5.031 calories/mole-degree. All values are for 300°K with the exception of oxygen which is for 298.1°K. Since the experimental temperatures never differ by more than 8° from these values it was unnecessary to correct the heat capacities for temperature.

At the lower pressures incomplete surface saturation of the wire is quite probably responsible for the low accommodation coefficient values. It seems well established[11] that the accommodation coefficient on a gas free wire is very much lower than that on a gas covered wire. In the present case the low values increase with pressure until they become constant at pressures sufficiently high to insure the presence of a monomolecular gas film on the platinum wire. The lowest pressure at which such surface saturation is attained will not be the same for each of the gases. It appears from Table I, however, that in all cases the accommodation coefficient no longer tends to increase at pressures above about 0.1 mm. Therefore, values below this pressure are placed in parentheses and have been omitted in computing the mean accommodation coefficients (and corresponding probable errors) characteristic of a gas saturated platinum wire. In the case of several gases where measurements were extended to relatively high pressures, there are indications of a decrease in the accommodation coefficient which may be due to the fact that energy transport by the gas is no longer entirely due to free molecule conduction as the mean free path becomes shorter. These values are also enclosed in parentheses and have been excluded in computing means. It should be pointed out that the inclusion of these few high pressure values or the assignment of slightly different values to the pressures at which surface saturation is definitely established would produce changes of at most a few tenths of a

[8] Reference 7, Vol. 5, p. 221 (first set of values).
[9] Reference 8, p. 243.

[10] (a) Hydrogen, C. O. Davis and H. L. Johnson, J. Am. Chem. Soc. **56**, 1045 (1934); (b) deuterium, H. L. Johnson and E. A. Long, J. Chem. Phys. **2**, 389 (1934); (c) nitrogen and carbon monoxide, C. O. Davis and H. L. Johnson, J. Am. Chem. Soc. **56**, 271 (1934); (d) oxygen, H. L. Johnson and M. K. Walker, *ibid.* **55**, 172 (1933).
[11] J. K. Roberts, Proc. Roy. Soc. **A129**, 146 (1930); **A135**, 192 (1932); **A142**, 519 (1933). W. B. Mann, *ibid.* **A146**, 776 (1934). W. B. Mann and W. C. Newell, *ibid.* **A158**, 397 (1937). B. Raines, Phys. Rev. **56**, 691 (1939).

percent in the tabulated mean values of the accommodation coefficients. The important function of the parenthetical entries is to emphasize the fact that the useful pressure range for determining accommodation coefficients on gas covered wire by the present method will in every case be limited by the necessity of having pressures high enough to insure surface saturation of the wire and at the same time low enough to insure complete free molecule conduction.

The values of Table I, particularly those for helium, show that, within the experimental error, the mean accommodation coefficient for each of the gases may be considered as constant in the temperature interval 19°–30.5°C.

The recent results of Thomas and Olmer have already been mentioned in connection with the necessity for extending measurements into the pressure range which insures surface saturation of the wire. In the calculation of their accommodation coefficient values they seem to have made an error which, together with their use of pressures below 0.05 mm, renders meaningless any comparison between their values and those of Table I. In their experiments the wall of the gauge was thermostated at 30°C and accommodation coefficients determined at a series of wire temperatures extending, in some cases, to about 400°C. For each gas they obtain a value for the accommodation coefficient at 30°C by extrapolation to zero temperature difference between wire and wall. Unfortunately, in their expression for the quantity of energy removed per second at unit pressure by free molecule conduction they use the absolute temperature of the wall, 303°K, instead of the absolute average temperature of the gas. This is equivalent to assuming that the gas which conducts heat from the wire to the wall has a density characteristic of the wall temperature rather than the average temperature between wire and wall. It has been previously pointed out that this average temperature is a function of the accommodation coefficient on the wire (when the accommodation coefficient on the wall may be taken as unity), the wire temperature, and the wall temperature. Using the accommodation coefficients reported by Thomas and Olmer, the average absolute temperature of the gas when the wire is at 330°C is 334°K for hydrogen ($a=0.22$) and 415°K for mercury ($a=1.00$). For gases with intermediate accommodation coefficients the average absolute gas temperature will lie between these values for the same temperature difference between wire and wall. Although the square root of the average absolute temperature appears in the free molecule conduction expression, the high temperature differences existing in the apparatus of Thomas and Olmer may result in serious errors when the accommodation coefficients are computed using incorrect values for the average absolute temperature of the gas. For example, the accommodation coefficient of mercury derived from measurements with a wire temperature of 330°C should be multiplied by $(415/303)^{\frac{1}{2}}$. In general all the accommodation coefficients of Thomas and Olmer calculated from experimental measurements are low, the magnitude of the error increasing with the temperature difference between wire and wall.

The features of the present method of measuring accommodation coefficients which are of particular importance may be summarized as follows.

By limiting the average temperature difference between the wire and walls to about 2°, it is possible to assume that the total emissivity and the thermal conductivity of the platinum are constant over the wire length and that the rate of energy loss by radiation is proportional to $T_0^3\Delta t$ without affecting by more than 0.1 percent any single accommodation coefficient in the useful pressure range. By including in the Wheatstone network a compensator in thermal contact with the gauge walls it is possible to keep practically constant the average temperature difference between the wire and walls at bridge balance. For example, when the wall temperature changes from 18.9° to 30.5°C, the average temperature difference between the wire and walls changes by only 4 percent, from 2.060° to 2.148°. Moreover, in any given case the magnitude of this small change can be exactly calculated. Finally, by confining the platinum wire between parallel plates only $\frac{1}{8}$ inch apart, it is possible to use pressures sufficiently high (while still maintaining complete free molecule conduction) to insure that the resulting accommodation coefficients refer to a gas saturated wire and not to a wire on which the extent of adsorption is unknown.