A STUDY OF GASEOUS EFFUSION AT HIGH TEMPERATURES*

By F. Russell Bichowsky and Channing W. Wilson

Abstract

An apparatus has been constructed and described for investigating the effusion of gases through a small orifice, and the method has been applied to helium between the temperatures of 1000° and 2000°K, and at pressures from 0.2 to 0.8 mm of mercury. The kinetic theory applying to the problem is discussed. It has been found that the effusion of the monatomic gas helium follows Knudsen's expression

$$N=PAN_L/(2\pi mkT)^{1/2}$$

Keeping the rate of flow constant, i.e., $N=N_0$,

$$P=P_0(T/T_0)^{1/2}$$

if allowance is made for viscosity and slippage effects of the gas in the orifice chamber. It is suggested that the apparatus may be used to measure high temperatures as a gas thermometer. Experiments were carried out with hydrogen at temperatures from 1000° to 1900°K, but an interpretation of the results is not possible because of the presence of both molecular and atomic hydrogen in the orifice chamber at these temperatures.

Introduction

In a paper by Weide and Bichowsky[1] a method was outlined by which the behavior of gases at very high temperatures and the course of some gaseous reactions could be studied. The method is based on the rate of effusion of a gas through a small orifice, in a manner similar to that used in many experiments by Graham,[2] Bunsen,[3] Meyer,[4] and Knudsen.[5] Recent applications have been made by Rodebush and DeVries[6] and Chopin.[7] Copeland and Bichowsky[8] measured the percent dissociation of hydrogen drawn from a discharge tube by a more extended form of the method.

Before attempting to apply the method to the dissociation of hydrogen at high temperatures it was found necessary to understand better the behavior of a simple gas in the apparatus. Therefore helium was selected and studied in the temperature range 1000°—2100°K. The results obtained with helium, and its application to gas thermometry at temperatures higher

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[1] Weide and Bichowsky, J. Amer. Chem. Soc. **48,** 2529 (1926).

[2] Graham, Phil. Trans. **136,** 572 (1846).

[3] Bunsen, Gasometrische Methoden Braunschweig, 2nd edition 1857, p. 127.

[4] Meyer, Kinetische Theorie der Gase, Breslau, 1877, p. 49.

[5] Knudsen, Ann. d. Physik **28,** 999 (1909).

[6] Rodebush and DeVries, J. Amer. Chem. Soc. **49,** 656 (1926).

[7] Chopin, Compte. Rendus. **186,** 1830 (1928).

[8] Copeland and Bichowsky, J. Amer. Chem. Soc. **60,** 1315 (1928).

than heretofore obtained with such instruments, as well as preliminary observations of hydrogen are included in this paper.

The method is based on Knudson's[5] expression relating the pressure of a gas and the number of molecules passing through a small orifice. This expression is

$$N = PAN_L/(2\pi mkT)^{1/2} \tag{1}$$

where N is the number of molecules of gas escaping through the orifice into a vacuum in unit time; P is the pressure of the gas in the orifice chamber in absolute units; A is the area of the hole in cm,^{2} N_L is Avogadro's number; m is the mass of the molecule; k is Boltzmann's constant, and T the absolute temperature.

If the rate of flow is kept constant (i.e. $N = N_0$) the pressure will vary with the absolute temperature

$$P = P_0(T/T_0)^{1/2} \tag{2}$$

where P is the pressure at any temperature T, and P_0 is the pressure at T_0, e.g. room temperature. Thus the method may be applied to measuring high temperature as a gas thermometer by observing the increase in orifice-chamber pressure when the temperature is raised. In this investigation helium was selected, because it is monatomic and non-corrosive under all conditions.

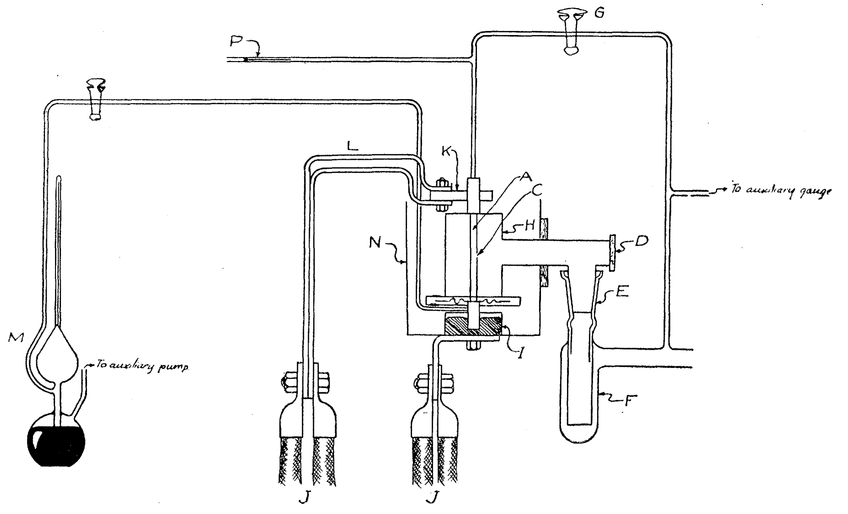

Fig. 1. Diagram of apparatus.

The method may best be explained by reference to Fig. 1. Helium is admitted to the tubular orifice chamber A through capillary P. It passes through the small hole C into a vacuum maintained in the steel jacket, H, by a mercury pump and an oil pump. The capillary is of such a size that the pressure of the gas at room temperature is a few tenths of a millimeter of mercury. The pressure is measured with a cathetometer on an accurately calibrated McLeod gauge, *M*. After a state of steady flow has been reached at room temperature the orifice-chamber tube is heated electrically to a high temperature. After a state of equilibrium is again reached the pressure corresponding to this temperature is measured. The temperature of the orifice is determined with an optical pyrometer by sighting through the glass window, *D*, directly at the hole. The pressure measurements are corrected for thermal effusion due to the temperature gradient along the tube, and the corrected pressures compared with those calculated for the high temperature by means of Eq. (2). The observed pressures and temperatures are plotted to give a calibration curve for the gas thermometer.

DESCRIPTION OF FURNACE

In this apparatus the helium was heated in the tubular orifice chamber, and the arrangement may be seen from Fig. 1. The orifice-chamber tube, *A*, was machined from molybdenum (m.p. 2898°K),[9] 10 cm in length, 0.475 cm internal diameter, with a wall 0.8 mm thick. The orifice, *C*, was drilled in the wall 5 cm from the end, and was 0.38 mm in diameter. The hole was then given a taper with the point of a larger drill, so that it was, in effect, a hole in a thin wall, and not a short tube. This is a necessary condition upon which Eq. (1) is derived. On each end of the molybdenum tube a steel terminal piece was welded to provide for electrical connections, and for the inlet of gas and connection to the McLeod gauge.

The tube was located axially in a steel vacuum-jacket *H*, and was provided at one end with a corrugated disk to take care of the linear expansion of the tube when it was heated. An observation tube was welded to one side of the vacuum jacket opposite the orifice so that the temperature of the hole could be determined optically through window *D*. This tube served also as a vacuum line, and was connected to a two-stage Stimson mercury pump through a ground-glass joint *E* and liquid-air trap *F*. During operation the vacuum-jacket was cooled in a large water bath *N*. Its temperature never rose above 50°C, even when the tube within was at 2000°. A Nelson oil pump was used to obtain a fore-vacuum.

The pressure gauge *M* differed from the usual type of McLeod gauge in that it had a long capillary stem, and had no compensating capillary side-arm. Capillary depression was corrected for in the measurements, which were made with a cathetometer.

Power for heating the orifice-chamber tube was obtained from a 15 K. V. A. motor-generator set, through a step-down transformer. The voltage applied to the tube was adjusted by varying the current in the generator field. A maximum of 10 volts could be used.

The temperature of the orifice was obtained by assuming it to be a black-body radiator, and matching its brightness with the filament of an optical pyrometer which had been certified by the U. S. Bureau of Standards. The temperature thus obtained was the actual temperature of the gas as it escaped from the orifice.

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[9] Worthing, Phys. Rev. **28**, 190 (1926).

THEORETICAL

When a non-dissociating gas, such as helium, is admitted to the apparatus, Eq. (2) will be followed, provided the pressure measured on the gauge is the pressure of the gas at the orifice. This condition is fulfilled in the measurements taken at room temperature, because the entire orifice-chamber is at the same temperature, which is also the temperature of the McLeod gauge. Consequently, the gas is at the same pressure throughout the chamber and gauge.

The conditions are different, however, in the high temperature runs. The temperature measured with the pyrometer is the temperature of the gas at the orifice, but there is a temperature gradient along the orifice chamber tube, and the temperature at each end is that of the water in the cooling bath. Since the gas in the tube may be considered nearly stationary, a pressure gradient results from this difference in temperature, and the pressure measured on the gauge will be the pressure of the gas in the cool portion of the tube. The pressure measured on the gauge must therefore be corrected for thermal effusion, so that the pressure of the gas at the orifice at high temperatures may be obtained. The differences between the measured values and the pressures calculated for the high temperatures by means of Eq. (2) are obviously due to viscosity effects which must be accounted for mathematically, although no data are available at temperatures higher than 300°C.

The equation for the flow of gas through a tube, whose diameter is large in comparison with the mean free path of the molecules, has been derived by Maxwell,[10] which is, for the most general case involving both temperature and pressure gradients

$$\frac{dn}{dt}=\frac{1}{8\eta L}\,\frac{(1+8\eta)\pi d^4(p_2{}^2-p_1{}^2)}{\eta_\alpha d32RT}-\frac{M}{\pi}\left(\frac{dn}{dt}\right)^2-\frac{\pi d^2 3\eta}{16M}\,\frac{1}{T}\,\frac{\partial T}{\partial x} \tag{3}$$

This equation gives the number of mols of gas passing through a cross-sectional area of the tube per second, where L is the length of the tube; η is the viscosity of the gas; η/η_α the coefficient of slip; d is the diameter of the tube in cm; R is the gas constant per mol; $p_2{}^2-p_1{}^2$ is the difference of the squares of the pressure at each end of the tube in C. G. S. units; T is the absolute temperature; and M is the molecular weight of the gas. The last term in the equation represents the flow due to the temperature gradient.

For a stationary state in which there is no flow, the right hand side of the equation may be equated to zero, and there is then obtained

$$\frac{dp^2}{dT}=\frac{12\eta^2R}{M}\,\frac{1}{(d^2/4)+(2\eta d/\eta_\alpha)}\,. \tag{4}$$

This equation gives the rate of change of pressure with the temperature along the tube.

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[10] Maxwell, Phil. Trans. **170**, 231 (1880); Scientific Papers 2, 681 Cambridge (1890). See also Herzfeld, Kinetische Theorie der Wärme.

It is possible to perform a graphical integration over the curve of the temperature gradient by assuming that for small temperature differences it is a straight line whose slope is that of the midpoint of the interval. For this purpose the viscosity of the gas, η, must be known as a function of the temperature, and the coefficient of slip of the gas along the walls of the tube must be evaluated.

It was assumed that for helium the viscosity varies with the temperature according to the equation[11]

$$\eta = \eta_0 T^{0.65}/273.1$$

where η_0 is the coefficient of viscosity at 0°C, $= 1891 \times 10^{-7}$ [12]and the curve of the equation $\eta^2 = f(T)$ was plotted. For the graphical integration of Eq. (4), temperature intervals of 100° were used, beginning at 300° and ending with the observed temperature of the orifice. Therefore values of η^2 for substitution in the expression were interpolated from the curve for the mean temperature of each interval, i.e., 350°, 450°, 550°K etc. The pressure term in the denominator was given the value of the pressure, in absolute units, at the beginning of the interval.

For the coefficient of slip, Epstein[13] gives the expression

$$\eta/\eta_\alpha = 0.7004\Lambda(2-f)/f \tag{5}$$

where Λ is the free path of the gas molecules, and f is the so-called "accommodation" factor,[14] representing the fraction of the molecules not reflected from the walls of the tube according to the laws of reflection of elastic spheres, but which may be considered to be "emitted" from the walls.

The free path at any temperature, T, may be represented by Sutherland's[15] formula

$$\Lambda = \Lambda_\infty/(1+c/T)$$

where Λ_∞ is the free path at $T=\infty$, and at the density corresponding to atmospheric pressure; c is Sutherland's constant. Substituting in Eq. (5) gives

$$\frac{\eta}{\eta_\alpha} = 0.7004\frac{2-f}{f}\cdot\frac{\Lambda_\infty}{1+c/T}\cdot$$

Inserting this in Eq. (4) and reducing to a form more convenient for computation

$$\frac{dp^2}{dT} = \frac{12R\eta^2}{Md/2}\left[\frac{d}{2} + 2.8016\frac{2-f}{f}\cdot\frac{\Lambda_\infty}{1+c/T}\cdot\frac{T}{p}\cdot\frac{760}{273}\right]^{-1} \tag{6}$$

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[11] Kammerlingh-Onnes and Weber give the exponent to be 0.647, while Rayleigh gives 0.681. The value 0.65 was selected here because it fit our data best.

[12] Landolt-Börnstein, Tabellen, 5th edition, Berlin 1923, p. 172.

[13] Epstein, Phys. Rev. **23,** 710 (1924).

[14] This is the assumption made by Knudsen, Maxwell and Smoluchowski, to account for the experimental observations on slippage. Maxwell, reference 10; Knudsen, Ann. d. Physik **28,** 75 (1909); **35,** 389 (1911); Smoluchowski: ibid **33,** 1559 (1910).

[15] Sutherland, Phil. Mag. (V) **35,** 507 (1893).

Using $d=0.476$ cm; $f=0.74$[16]; $\Lambda_\infty=2.201\times10^{-5}$ [15] and $c=70$[12] the expression becomes

$$\frac{dp^2}{dT}=\frac{12R\eta^2}{0.238M}\left[0.238+\frac{(5904.9\times10^{-5})T}{202.02(1+c/T)p}\right]^{-1}$$

For each pressure measurement with helium the calculations were carried out and the correction curves were plotted. The similarity of the correction curves eliminated the possibility of a serious accidental error entering. The pressure of the gas at the orifice at the high temperature may be found by either graphical or arithmetical interpolation of the correction curve. In all experiments it was computed by the latter method and checked by the former.

EXPERIMENTAL DATA

Experiments were carried out by admitting helium to the apparatus as previously described. These were divided into two series; the first with orifice chamber pressures, at room temperature, in the neighborhood of 0.24 mm, and the second having initial pressures of about 0.4 mm. In both series the complete temperature range, through which the optical pyrometer could be used, was covered. The data obtained are recorded in Tables I and II. The first column of the tables gives the mean initial temperature, T_0, and in the next column the orifice-chamber pressures, P_0, observed when a steady state was reached at this temperature, are recorded. The third column gives the mean temperature of the orifice, T_1, measured with the pyrometer. The fourth column gives the pressures, which should prevail at the orifice at temperature T_1 if Eq. (2) is followed. The fifth column gives the steady

TABLE I. *Results with helium. Series I.*

T_0	P_0	T_1	P_{calc}	P_{obs}	P_{cor}
290.5	0.267	1185	0.541	0.430	0.535
291.7	0.242	1299	0.512	0.414	0.529
290.4	0.249	1447	0.557	0.395	0.553
291.5	0.248	1549	0.572	0.389	0.567
291.5	0.241	1616	0.566	0.377	0.566

TABLE II. *Results with helium. Series II.*

T_0	P_0	T_1	P_{calc}	P_{obs}	P_{cor}
287.5	0.414	1147	0.827	0.761	0.841
288.1	0.410	1281	0.865	0.754	0.869
287.8	0.449	1543	1.036	0.871	1.021
290.7	0.471	1810	1.177	0.930	1.160
287.5	0.339	2015	0.897	0.676	0.904

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[16] Millikan, Phys. Rev. (II) **21,** 217 (1923), gives f the value 0.875 from results of his study of oil droplets in helium. However, the value is probably smaller for the action between helium and molybdenum, and if a value 0.74 is assumed the data obtained here best fit the equation. This makes the factor $(2-f)/f=1.7$.

state pressures actually observed at the high temperature, and the last column gives the corrected value when Eq. (6) is applied to these observations. All pressures are in mm of mercury, and temperatures in degrees K.

The results of the experiments are also shown graphically in Figs. 2 and 3 respectively for Series I and II. In order to have comparable results for plotting, the pressure measurements were all proportionately reduced to the value they would have had if the initial pressure at room temperature

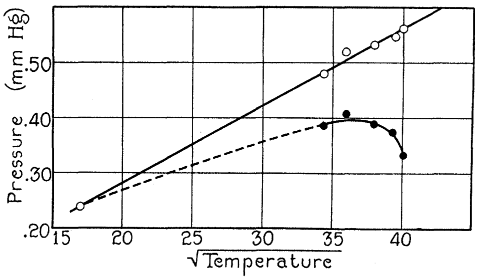

Fig. 2. Helium series I. Pressure-temperature curves.

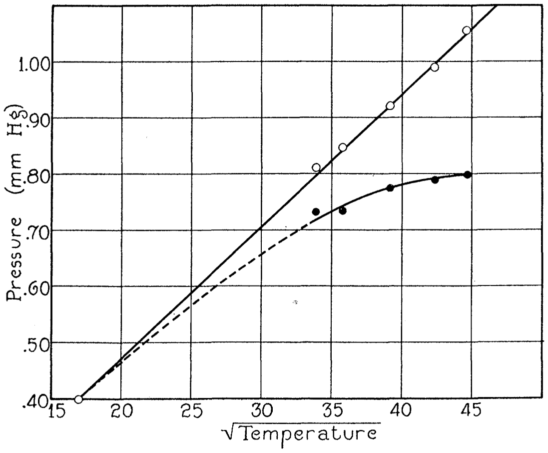

Fig. 3. Helium series II. Pressure-temperature curves.

during all experiments of Series I had been 0.24 mm and the initial pressure at room temperature in Series II had been 0.4 mm. These values were then plotted against $T^{1/2}$. The straight line in each graph gives the theoretical values of the pressure at any temperature calculated by means of Eq. (2). The black circles show the observed pressures reduced as just described. The dotted curves are extrapolations of the observed curves to room temperature. It must pass through the point on each curve representing the initial pressure at room temperature, because the correction factor on the right side of the Eq. (6) vanishes when the temperature of the orifice-chamber tube is uniform. The open circles represent the values of P_{cor} reduced proportionately as described.

DISCUSSION OF HELIUM RESULTS

Probably the largest sources of error involved in the measurements are: (1) high temperature measurements with the optical pyrometer, (2) steady-state not reached and (3) errors involved in viscosity data used.

The pyrometer lamp was calibrated by the Bureau of Standards to ±0.5 percent. However, the uncertainty in judging the intensity match at the upper and lower limits of the range may be probably such that in these regions an error of one percent greater may be found. This difficulty was caused by the low intensity of the black-body source near the lower limit of the range, and the high intensity of the filament near the upper limit of the range. Fortunately it was not necessary to perform many experiments in these regions.

It is possible that in some cases a steady state was not reached. The method of determining the steady state pressure was to assume that such a condition had been reached when three consecutive pressure measurements, taken at half-hour intervals, agreed to within the accuracy of reading the McLeod gauge. This was estimated to be within ±0.1 percent. However, because of the conditions under which the helium was supplied to the orifice chamber, it was not possible to check the steady state pressure at room temperature after a high temperature run.

Besides these possible experimental errors, the corrections made for viscosity and slippage might be inaccurate. Values given in the literature for the viscosity of helium at 0°C, and its variation with temperature, as well as for the factor f in Eq. (5) differ by several percent. It is true that these errors enter only in the correction factor, but their effect is cumulative. However, their effect will be the same on all data, that is, they will give either too large or too small a correction to all measurements. Therefore, a proper choice of values for η and f can be made, and those which fit one set of data should fit all.

In the experiments of Series I, the maximum deviation from the theoretical value is +3.3 percent, found at 1299°K, which is near the lower limit of observable temperatures. In the measurement made at 1549°K, which is near the upper limit of the lower range of the pyrometer, an error of −2.1 percent was observed. In the five experiments of this series the average deviation is −0.1 percent.

In Series II the maximum error is +1.6 percent, and the maximum negative error is −1.5 percent. The average of all positive and negative errors is zero. The maximum errors lie in the same pyrometer regions as those in Series I.

It is apparent from these results that if the instrument is to be used as a gas thermometer at high temperatures it would be advantageous to use as high orifice-chamber pressures as possible, since in these the percent error in the measurement of pressures is less, and also the corrections are less. However, in order to use higher pressures, the proper procedure would be to decrease the diameter of the orifice, and not to increase the rate of flow of the gas through the capillary. By the latter procedure the density in the orifice chamber would become so great that equation (1) would be invalidated by the decrease in free path of the molecules. However if the pressure is increased by decreasing the diameter of the orifice it should be possible to make the curve of observed pressures approach very near to the theoretical curve. This may be seen by comparing the curves of Figs. 2 and 3.

The experimental results obtained with helium indicate that the theory of effusion through small holes is valid at high temperatures when suitable corrections are entered for the effects due to viscosity and slippage. Therefore it is possible to use the instrument which has been described, as a gas thermometer for temperatures up to 2000°K. In order to do this practically, however, it would not be necessary to know the proper correction factors, but with a fixed initial pressure at room temperature it could be calibrated at two other points to determine the curve of observed pressures, which would then be used as a temperature scale. Or if the viscosity and slippage factors are known for the gas which is used the curve of observed pressures can be calculated without an experimental determination, if the initial pressure is known.

APPLICATION OF THE METHOD TO HYDROGEN

An attempt was made to use hydrogen in the apparatus, in order to study its thermal dissociation, and it was calculated that observable effects due to the dissociation would begin at about 1100°K.

Experiments showed that up to about 1180°K, this gas behaved in a manner entirely similar to helium, and that the data could be interpreted when viscosity and slippage factors were considered. However, above this temperature the results were inconclusive because of the presence of hydrogen atoms. It would be necessary to evaluate the viscosity of the hydrogen atoms, as well as their coefficient of slip in the molybdenum tube. Since the pressure factor enters in the denominator of the viscosity correction Eq. (6), it would also be necessary to have an approximate knowledge of the partial pressures of the molecules and atoms at each temperature. Then the total correction to be added to the observed pressure measurements would be the sum of the correction due to the viscosity of the molecules present and that due to the viscosity of the atoms.

With these uncertainties to overcome it is obvious that the data obtained could lead to no definite conclusions concerning the dissociation of hydrogen.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
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