

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

METHODS FOR STUDYING EFFUSION OF GASES¹

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The rate of effusion of a pure gas through a small hole into an evacuated space depends only on the mean component of velocity of the molecules of the gas in the direction of the hole and on the number of molecules per cubic centimeter having that velocity. The exact equation² is

$$N = (N_0 P S t) / \sqrt{2\pi k m T}$$

In this equation N is the number of molecules passing through the hole in t seconds; P is the pressure of the gas in dynes per square centimeter. N_0 is Avogadro's number (for a cubic centimeter); T is the absolute temperature in the mass of a single molecule and S the area of the hole in square centimeters. Since all the quantities in this equation are known or can be measured to high accuracy and since the equation is a simple consequence of the kinetic theory, methods of studying gases based on this equation should be capable of high accuracy provided only the experimental conditions are those assumed in the derivation of the equation. These are: (1) the pressure on the evacuated side of the hole is small in comparison with that on the high-pressure side; (2) the hole is small in comparison to the mean free path of the gas; (3) the thickness of the plate in which the hole is made is small in comparison with the diameter of the hole; (4) the chamber on the high-pressure side of the plate is large in comparison with the mean free path of the gas; (5) the gas on the high-pressure side is in thermal and pressure equilibrium over a region in the neighborhood of the hole which is large in comparison with the mean free path of the gas. In practice all of these conditions can be met well enough so that the small correction due to slight deviations from ideal conditions can be calculated to sufficient accuracy by formulas based on the theory of mean free path.³

The most familiar application of this equation is Graham's law,⁴ namely, the rate of flow of two gases through a given orifice at the same constant pressure and temperature is proportional to the inverse square root of the molecular weight. Previous studies of this law have been made with gases at such pressure, and with orifices of such size that viscosity of the gas is by no means negligible. Under these conditions the law can hold only

¹ This paper is an abstract of a thesis presented by Herbert Weide in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Johns Hopkins University.

² Jeans, "The Dynamical Theory of Gases," Cambridge Univ. Press, Cambridge, England, 4 Ed., 1925, p. 121.

³ Knudsen, *Ann. Physik*, **28**, 75, 999 (1909).

⁴ Graham, *Phil. Trans.*, **136**, 573 (1846).

approximately excepting for gases of the same viscosity. Thus Bunsen⁵ using a porous plate as an orifice and Graham⁴ using both porous plates and small holes found the apparent molecular weight of hydrogen (viscosity, 0.000086) as compared with air (viscosity, 0.000173) to be about 2.2, and that of carbon dioxide (viscosity, 0.000139) to be about 42.

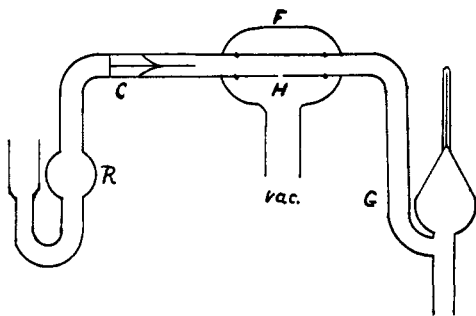


Fig. 1.

The scheme of our apparatus is shown in Fig. 1. It consisted of a rate-measuring device R, a capillary C of small enough bore so that a desired rate of flow could be obtained, a furnace F for heating the slowly flowing gas to a desired temperature, the small hole H leading into the evacuated system, and the pressure gage G for measuring the pressure in the gas stream at H.

In our first experiments various rate-measuring devices were tried but discarded for the reason that slight variation in pressure of the gas at the intake, introduced during a reading, produced irregularities in the rate of flow through the capillary which would not be ironed out, at least for long capillaries containing the enlargements necessary for sealing them together, for surprisingly long periods (in one case an hour). Eventually we discarded any special rate-measuring device on the high-pressure side of the capillary and calculated the rate from the increase of pressure in the system for a given time, the part of the system containing the hole being cut off from the rest of the apparatus. Since, under our conditions, the rate of flow through the capillary is very nearly independent of the pressure on the low-pressure side, this is a very convenient method and requires for high accuracy only accurate measurement of the volume of the pressure-measuring system, which is most easily obtained by calibration with a known volume of gas. However, it is possible to reduce the error greatly due to disturbance of steady-state conditions by using the short capillaries shown in Fig. 2 instead of the long ones actually used in the first experiment.

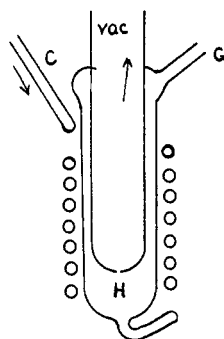


Fig. 1a.

In the first experiments the "furnace" was in the form of Fig. 1a. In this form the region of the hole and the inflowing gas could be kept at constant temperature with an ice- or vapor-bath. The McLeod

⁵ Bunsen, "Gasometrische Methoden," Vieweg. u. Sohn. Braunschweig, 1877, p. 189.

gage was of the usual type except that the second capillary tube customarily used to correct automatically for the capillary depression of the mercury in the calibrated stem was omitted. This omission reduces by one-half the uncertainty due to the partial sticking of the mercury in the capillaries but, of course, necessitates correcting the measured differences of level by the capillary depression of the small tube. This correction can be measured accurately during the calibration of the gage and introduces no error. In our first experiment the hole had a diameter of 0.011 ± 0.002 cm., the pressure chamber a volume of 1 cc.; the inlet tube a diameter of 0.3 cm., the outlet tube 1.2 cm. (both of which diameters are smaller than desirable). The data for our runs on hydrogen and dry air follow: Air: $P = 0.07754$ cm. of Hg; $t = 14' 50''$; volume of pipet, $v = 1.00$ cc.; $T = 301.1^\circ$; barometric pressure, $B = 76.014$ cm. of Hg; hydrogen, $P = 0.04292$ cm. of Hg; $t = 7' 7''$; $v = 1.00$; $T = 301.1^\circ$; $B = 76.001$. Using Graham's law, the calculated molecular weight of hydrogen is 2.048, that is, if air is assumed to have the composition in mole fractions $N_2 = 0.7803$, $O_2 = 0.2099$, $A = 0.0094$, $CO_2 = 0.0004$ and therefore the equivalent mean square molecular weight of 28.88. Under these conditions hydrogen has a mean free path of about 0.02 cm.

Another method of comparing our results is to calculate the size of the orifice from data on the two gases. In the units employed, the radius of the hole supposed to be a true circle is given by the equation $r^2 = 0.000024916 v \sqrt{TM/tP}$ or, using our data, $r_{H_2} = 0.00534$, $r_{air} = 0.00536$; measured, 0.0055 ± 0.0010 .

A less familiar application of our method is the measurement of temperatures. For constant rate of flow, constant hole size and for a gas that does not dissociate, the pressure should be directly proportional to the square root of the absolute temperature. Under our conditions this law should be accurately followed even at very high temperatures. There is, however, a precaution in the interpretation of our equation which is necessary at this point. The pressure P which occurs in our equation is the pressure of the gas in the region around the hole and even for a stationary column of gas such as we have in the pressure measuring line, this is not necessarily equal to the pressure at other points of the column if these points are at different temperatures. For tubes that are small relative to the mean free path, the ratio of pressures in parts of the tube having different temperatures is in fact that given by our equation, $P_1/P_2 = T_1/T_2$. This effect, known as thermal effusion, varies for this extreme value to zero

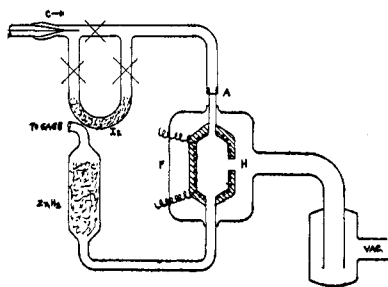


Fig. 2.

under different conditions.⁶ Under conditions in which thermal effusion occurs, the pressure as measured in the McLeod gage will be lower than the pressure in the region of higher temperature near H by an amount which in the limit would be just sufficient to make the reading at the gage independent of the temperature at H . If, however, the mean free path of the gas in the region of thermal gradient is small in comparison with the diameter of the tube in that region, and if the mean free path is also small in comparison with the temperature gradient, each molecule will make many collisions before reaching a region of different temperature, and pressure equality will be established in all parts of the tube. Under these conditions the McLeod gage at room temperatures will measure the pressure P of the region near H . The intermediate case is of interest for the experimental study of mean free path but its theory will not be attempted here.

Experiments with Apparatus 1a show that the ideal condition of no thermal effusion can be approached closely in practice. In these experiments the McLeod gage was used as a constant-volume instrument, that is to say, the mercury in the stem was brought to a fixed mark for each experiment, but their constancy was assured by using one-half of the capillary as a flow meter; the slight differences in pressure indicated on this flow meter between different runs was proportional to the change in the barometer and was assumed to be proportional to the corresponding rates of flow. The gage was not thermostatted in these experiments and the chief error is probably in its temperature.

TABLE I
EXPERIMENTS AT DIFFERENT TEMPERATURES

Bath	Ice	Steam	Naphthalene vapor
Mark on stem.....	No. 6	No. 6	No. 6
Pressure difference, mm....	273.0	319.7	364.8
Capillary depression.....	2.4	2.4	2.4
Barometer.....	759.4	759.4	760.1
Temperature of gage °C....	28.0 ± 0.3	29.2 ± 0.3	27.4 ± 0.3
Temperature of bath °C....	0.0	100.0	217.3
Calculated temperature °C.	(00) ± 0.4	100.0 ± 0.6	217.9 ± 1.0

That the equation holds at higher temperatures will be shown in another connection.

The chief interest of these methods is their joint application to the measurement of degree of dissociation of gases at high temperatures. If a gas dissociates in the region near the hole according to the equation $A_2 = 2A$, the various molecular species will escape at a rate that is the sum of the rates at which they would escape at that temperature if present in a pure form at the pressure of their partial pressure in the mixture, that is,

$$N = N_{A_2} + \frac{1}{2}N_A = \frac{P_{A_2} + \frac{1}{2}P_{A_2}}{\sqrt{2\pi kTm_{A_2}}}$$

⁶ Ref. 2, West, *Proc. Phys. Soc.*, **31**, 278 (1919).

In this equation N is the number of gas molecules of A_2 entering the capillary in the time t , N_{A_2} and N_A the number of the molecules of the species A_2 and A passing through the hole, P_{A_2} and P_A the partial pressures of A_2 and A . Substituting $P = P_{A_2} + P_A$ and writing our equation in such form that it shows the relative rates of flow through the same apparatus at temperatures T_0 (where there is no dissociation) and at T , where there is dissociation, and substituting $P_{\text{calcd.}} = P_0(N_1/N_0) \sqrt{T_1/T_0}$, we obtain $P_A = 3.41 (P - P_{\text{calcd.}})$ where P_A is the partial pressure of the product of dissociation, P the measured pressure and $P_{\text{calcd.}}$ the pressure calculated on the assumption of no dissociation.

Our method thus allows a sensitive and accurate measure of dissociation at relatively low pressures and temperatures. Our first experiments with hydrogen were terminated temporarily by an accident to the tube. We therefore, merely as a qualitative test of the method, ran one experiment with iodine, for which the value of the degree of dissociation is known sufficiently well from Bodenstein's excellent investigation of vapor densities to make more careful work unnecessary. In the case of hydrogen and other permanent non-corrosive gases, our apparatus was almost exactly as shown in Fig. 1, but for a solid or liquid whose vapor pressure is low and whose vapor reacts with mercury, as iodine vapor does, the modified apparatus shown in Fig. 2 was devised. The operation was as follows. A capillary C was chosen which would give at the steady state, an air pressure of about the magnitude of the iodine pressure expected. The apparatus was then run as a gas thermometer exactly as described previously. At various temperatures up to 1000° the operation was then repeated passing the air stream over the iodine which, of course, should be in a constant temperature bath whose temperature must be less than that of any point of the tube (A) to prevent deposition of iodine in that tube. At room temperature, the difference between these two readings should be the vapor pressure of iodine. That this is accurately so is shown by the following data: temperature, 25° ; P_{air} , 0.0318; P_{I_2} , 0.0297 (vapor pressure $\text{I}_2 = 0.0305$).⁷ Indeed the method seems a most promising one of measuring the vapor pressure of corrosive substances at not too low pressures, at least as convenient as the method of Knudsen based on a similar principle but which requires knowledge of the size of the hole, actual measurement of the loss of weight per unit time, and an assumption as to the molecular weight of the vapor; of course, in theory there should be a small correction for diffusion of gas down the measuring column of air (G) but by making this tube long and of small bore this correction is negligible for pressures of air down to 0.10 cm. The vapor trap T (in the case of iodine, amalgamated zinc) is necessary to prevent corrosive vapor being drawn into the pump during the manipulations at starting and stopping rather than

⁷ Baxter, Hickey and Holmes, *THIS JOURNAL*, 29, 127 (1907).

to prevent actual diffusion during the run. Having made the run with iodine at room temperature, the measurements were carried up to the higher temperatures, preferably exactly that of the air run. Preliminary results are: T (absolute) = 300° ; $P_{\text{air}} = 0.242$ mm.; $P_{\text{air}} + I_2 = 0.448$ mm.; $T = 908^{\circ}$; $P_{\text{air}} + I_2 + I = 0.825$ mm.; $T = 925^{\circ}$; $P_{\text{air}} + I_2 + I = 0.847$ mm.; $T = 1213^{\circ}$; $P_{\text{air}} + I = 1.580$ mm.

In these runs the temperature of the furnace was determined by a calibration using the instrument as a gas thermometer. This calibration checked that using a thermocouple to within a few degrees except at the higher temperatures where there was reason to suspect that the thermocouple (which was a very imperfect one) was at fault. We should have liked to check this calibration optically, but the necessary pyrometer was not available at the moment. The most serious source of error came from the fact that the water used to cool the furnace was at a temperature lower than room temperature and therefore it was suspected that iodine was being deposited at the point (A). There was, therefore, considerable chance of the partial pressure of the iodine in the cold gas changing with the temperature of the furnace. Indeed, at the higher temperatures the pressure change is higher than that calculated on the assumption of complete dissociation of the iodine. However, the results at about 915° lead to a value for $\log k$ of 3.7 (Lewis and Randall calculate 3.4 ± 0.2).

Summary

A new method of measuring the temperature and molecular weight of gases has been described. A preliminary determination of the dissociation constant of iodine at 740° has been made.

BALTIMORE, MARYLAND

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THE EQUILIBRIUM BETWEEN ZIRCONIUM OXIDE AND CARBON AND THEIR REACTION PRODUCTS AT INCANDESCENT TEMPERATURES

By C. H. PRESCOTT, JR.

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Plan of the Investigation

This research was begun in the fall of 1923 at the suggestion of Professor A. A. Noyes as an attempt to devise an apparatus and precision technique for the study of chemical equilibria at incandescent temperatures. The particular subject of interest was the investigation of the stability of refractory oxides. The reduction of zirconium oxide by carbon was chosen as the immediate subject for research.