DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 94

EFFUSION METHOD OF DETERMINING GAS DENSITY

BY

JUNIUS DAVID EDWARDS, Assistant Chemist
Bureau of Standards

ISSUED JUNE 20, 1917

PRICE, 10 CENTS
Sold only by the Superintendent of Documents, Government Printing Office
Washington, D. C.

WASHINGTON
GOVERNMENT PRINTING OFFICE
1917

EFFUSION METHOD OF DETERMINING GAS DENSITY

By Junius David Edwards

CONTENTS

1. INTRODUCTION

The effusion method of determining gas density has been in common use for over half a century in practically the same form as originally developed by Bunsen[1] and Schilling.[2] This method is based upon the fact that the times required for the escape of equal volumes of two gases under the same pressure through the same small orifice are approximately proportional to the square roots of the densities of the gases. Because of the advantages it offers in the way of simplicity and convenience of apparatus, this method has been employed in many lines of scientific and technical work where gas-density measurements were required. One of the most important uses has been in the natural-gas industry, where the measurement of gas by means of orifice meters requires a knowl-

[1] Bunsen, Gasometrische Methoden, p. 128; 1857.

[2] Schilling, Handb. d. Steinkohlengasbeleuchtung, 3d edition, p. 100.

edge of the density of the gas. During recent years many millions of dollars worth of natural gas has been bought and sold on the basis of such measurements. Frequent lack of agreement between the different users of this method has given rise to many controversies regarding the density of the gas being metered. Because of this unsatisfactory state of affairs the Bureau of Standards, at the request of certain gas companies, undertook an investigation in order to discover the sources of error in the method and to develop the apparatus and technique necessary to secure the best results.

It is desirable at this point to define density and specific gravity. The density of a gas is the mass of a unit volume measured under specified conditions of temperature and pressure. The term "specific gravity," as used in this paper, means the ratio of the weight of a given volume of gas to the weight of an equal volume of air, measured at the same temperature and pressure; the further limitation of this definition is discussed on page 15.

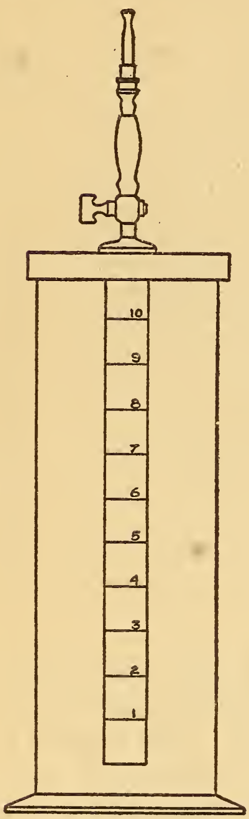

FIG. 1.—*Effusion apparatus used in preliminary tests*

2. PRELIMINARY TESTS

As a part of the investigation, a preliminary series of tests was made at the Bureau with the cooperation of a number of men experienced in the use of the method. The men cooperating with the staff of the gas laboratory were S. S. Wyer, T. H. Kerr, P. M. Biddison, H. T. Ashton, and T. R. Weymouth. These tests were designed to determine the accuracy of the method as used under field conditions by experienced observers.

The majority of the tests were made with two pieces of apparatus, one of which is illustrated in Fig. 1. The second apparatus was practically the same except that it had a three-way cock with a side outlet instead of the simple two-way cock shown in Fig. 1. In operation, the outer jar was filled with water to a certain level. The gas was introduced through the tube designed to carry the orifice, and the orifice slipped into the friction socket as quickly as possible after removing the gas delivery tube.

After opening the stopcock to start the effusion, a small amount of gas was allowed to pass through the orifice before beginning the observation in order to free the orifice tube from air. The time of effusion between graduations 2 and 8 or 2 and 9 was usually observed. The time was determined independently by two observers with stop watches. The average of the two results for each test is given in Table 1. The pressure at the start of each test was approximately 8 inches of water; that at the finish is given in the table.

TABLE 1

Preliminary Series of Tests with Effusion Apparatus

(a) Tests made with natural gas of specific gravity 0.752 (gas saturated with water vapor referred to saturated air at 20° C, 760 mm pressure)

Test	Orifice	Effusion pressure at finish (inches of water)	Apparent specific gravity	Error
				Per cent
1	13	2.0	0.695	− 7.6
2	13	0.5	.696	− 7.5
3	13	2.0	.704	− 6.4
4	13	0.5	.684	− 9.0
5	13	0.5	.671	−10.8
6	13	2.0	.648	−13.8
7	13	0.5	.687	− 8.6
8	4	2.0	.764	+ 1.6
9	4	2.0	.764	+ 1.6
10	4	2.0	.764	+ 1.6
11	4	2.0	.768	+ 2.1
12	4	2.0	.764	+ 1.6
13	4	2.0	.764	+ 1.6
14	4	0.5	.756	+ .5
15	1	2.0	.762	+ 1.3
16	1	0.5	.748	− .5
17	5	2.0	.739	− 1.7
18	11	0.5	.712	− 5.3
19	11	2.0	.721	− 4.1
20	11	2.0	.728	− 3.2
21	12	2.0	.754	+ .3

(b) Tests made with natural gas of specific gravity 0.650 (saturated gas referred to saturated air at 20° C, 760 mm pressure)

Test	Orifice	Effusion pressure at finish (inches of water)	Apparent specific gravity	Error
22	13	2.0	0.627	− 3.5
23	4	2.0	.657	+ 1.1
24	11	2.0	.634	− 2.5
25	12	2.0	.644	− .9
26	50	2.0	.629	− 3.2

The specific gravity of the gases used was carefully determined by the method of direct weighing described on page 8. The results are thus referred to a standard method of the required accuracy. From inspection of these data it is seen that results in error by as much as 13 per cent were obtained with one of the orifices tested. Not only were large variations observed when using different orifices, but the results obtained with the same orifice were in many cases erratic. The effect of changing certain conditions of operation was observed; for example, lowering the effusion pressure had a tendency to give lower results for the apparent specific gravity. H. T. Ashton had noticed the same effect in some experiments he had made with the effusion apparatus. When operating between the same pressure limits no differences assignable to differences in the instruments were found, so no distinction between instruments is made in the table.

No consistent improvement in accuracy was obtainable by several variations in the method of operation nor was any satisfactory explanation of the results forthcoming from a consideration of the theory of the effusion process as understood at that time. For further progress a better understanding of the theory was therefore necessary, and this phase of the problem was next investigated.

3. THEORY OF THE EFFUSION METHOD

The fact that the speeds of effusion of different gases are approximately inversely proportional to the square roots of their densities was empirically discovered by Graham[3] and others, and its use as a means of determining the specific gravity of a gas was suggested by him. On the basis of the kinetic theory of gases, the speed with which a gas will pass through a small opening (speed of effusion) must be proportional to the average speed of the molecules. Since the molecular speed of a gas is inversely proportional to the square root of its density, the rate of effusion is inversely proportional to the same quantity. The times (t) required for the effusion of equal volumes of different gases under equal pressures are therefore directly proportional to the square roots of the densities of the gases.

$$\text{Specific gravity} = \frac{d(\text{gas})}{d(\text{air})} = \frac{t^2(\text{gas})}{t^2(\text{air})}.$$

This theory assumes that the process is isothermal and that there is no loss of energy through friction in the orifice. At atmospheric pressure it is known that these conditions are not satisfied;

[3] Phil. Mag. (3), 2, p. 175; 1833.

the phenomenon is one of stream line flow and is affected by a number of factors of which the kinetic theory takes no account.

The effusion method is not concerned with the absolute rate of effusion of any gas, but only with the ratio of the rate of effusion of the gas and of air. For this reason it may be expected that deviations from the law will result from differences in certain physical properties of the gases, such as the ratio of the specific heats, the viscosity, the thermal conductivity, etc. However, because of the number of factors involved, the complete development of the theory has proven to be very difficult and a satisfactory correlation of all the variables has not yet been accomplished. It is desired at this time to present only the empirical relations between variables as shown directly by the experiments and leave to a later paper the theoretical discussion of these. The development of the theory has been done in collaboration with Dr. Edgar Buckingham of this Bureau.

4. EXPERIMENTAL APPARATUS AND METHODS

For the study of the influence of the numerous variables affecting the apparent specific gravity, gases of known specific gravity were used in different apparatus with different conditions and methods of operation.

(*a*) **Gases Used.**—Three samples of natural gas and one each of hydrogen, carbon dioxide, air, and argon were used. One of the natural gases was obtained especially for this work because of its high methane content (more than 90 per cent); it is referred to later in this paper as methane, since for this work it had substantially the characteristics of the pure gas. The hydrogen and carbon dioxide were from regular commercial supplies; the so-called argon was a mixture of 33 per cent argon with 46 per cent oxygen and 21 per cent nitrogen. The particular advantages of these gases for the work will be demonstrated in the later report on the theory of effusion.

The gases were stored in steel cylinders, the different samples of natural gas being confined at pressures up to 300 pounds and the other gases at pressures up to 1800 pounds. They were delivered from the cylinders at the proper working pressure by means of pressure regulators. In this way a sufficient supply of each gas, of constant composition, was available for use throughout the work. The gas was dried over phosphorous pentoxide before use except when using water as a confining medium in the apparatus.

(*b*) **Standard of Comparison.**—The density of the gas contained in each cylinder was determined by direct weighing of the gas in globes of 500 and 1000 cc capacity. These were closed by means of carefully ground, diagonal-bore stopcocks on the inlet tubes. The gas, after being carefully dried over sublimed phosphorous pentoxide, was introduced into the evacuated globe, and the globe was rinsed out once or twice with the gas before the final filling, in order to insure an uncontaminated sample. Before closing the globe preliminary to weighing, the temperature and pressure of the inclosed gas were determined. The temperature of the gas was controlled by immersing the globe in a water bath accurately controlled by a thermostat and the pressure in the globe was adjusted to that of the atmosphere at the instant of closing. The atmospheric pressure was determined by a standardized mercurial barometer close to the apparatus.

The weighing globe was then carefully wiped clean with a damp cloth and placed in the balance to allow it to come to equilibrium with its surroundings. To insure uniform temperature conditions throughout the balance, the glass balance case was surrounded by an almost air-tight copper box and this latter was inclosed in a light case of composition board. A counterpoise of the same shape and almost exactly the same volume as the globe was used in weighing. The necessary weights as determined by a preliminary weighing were placed upon the balance pan with the counterpoise when the globe was placed in the balance. From the time until the completion of the weighing the balance case remained closed. Usually 10 to 12 hours was allowed to elapse before beginning the weighing. During this time, a current of dry and dust-free air was passed through the balance case. A beaker containing highly radioactive carnotite was used to assist in dispelling any chance electrification. The weighing was made by the method of swings, observations being taken at regular intervals until constant weight was obtained. As the result of these precautions, the zero point of the balance remained very constant during any series of weighings.

The volume of the globe was obtained in the usual way by determining the weight of air-free water which it would contain. From the weight of the globe evacuated and its weight filled with gas the weight of the contained gas was obtained. A correction was applied for the contraction of the globe upon exhaustion, this change in volume having been experimentally determined in the usual manner; that is, by the change, upon evacuation, of the volume of water displaced. The usual correction for the buoyancy of the weights was also applied whenever significant, but no correction for the buoyancy of the globe was required because of the counterpoise used. The weight of 1 l of the gas at 20° and 760 mm was calculated from the above results and the specific gravity was taken as the ratio of this weight to the weight of a liter of air, determined in the same manner. The air used in most of the determinations was obtained from a cylinder of compressed air, the same sample being used throughout the work. The following example shows the data and calculations for the density of the hydrogen used:

Determinations of Density of Hydrogen (From Cylinder No. K21759)

Nature of data	Test No. I	Test No. II
Temperature (°C)	21.96	22.78
Pressure (mm)	760.9	761.4
Volume (cc)	960.9	960.9
Weight of hydrogen, uncorrected (g)	0.10188	0.10164
Correction for contraction of globe (g)	.00017	.00017
Correction for buoyancy of weights (g)	− .000005	− .000005
Weight of hydrogen (g)	0.10205	0.10181
Weight of liter at 20°, 760 mm	$=\frac{0.10205\times760\times294.96}{960.9\times760.9\times293}$	$=\frac{0.10181\times760\times295.78}{960.9\times761.4\times293}$
	=0.10679 g	=0.10676 g

Average weight per liter 0.10678
Specific gravity 0.0885

(*c*) **Effusion Apparatus.**—The apparatus used in the study of the variables of the effusion process is shown in Figs. 2 and 3. The apparatus shown in Fig. 2 was used especially for studying the effect of pressure upon the rate of effusion. It consists of a cylindrical chamber *G*, containing the gas, connected by a glass tube to the mercury reservoir *R*. The gas chamber was surrounded by a water bath, the temperature of which was observed by means of a thermometer suspended in it. A short length of heavy walled rubber tubing was inserted in the tube leading from the mercury reservoir, so that the latter could be closed off from the gas chamber by means of a pinch cock when it was desired to evacuate the apparatus. The rubber stopper closing the gas chamber carried the orifice tube and the tube for introducing the gas and air, as shown. The gas could be introduced at any desired pressure as previously explained.

84848°—17——2

An automatic electrical method of timing was used. A series of platinum contacts properly insulated on the outside were sealed into the walls of the gas chamber at approximately equal intervals. When the gas was effusing, the ascending column of mercury, closing the circuit at each terminal, recorded the time of contact

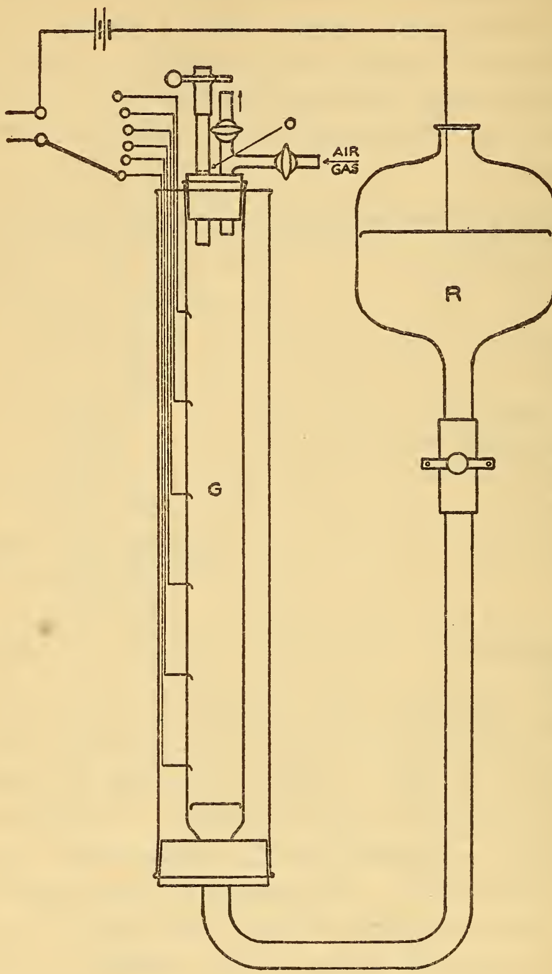

FIG. 2.—*Effusion apparatus with automatic timing system*

on a chronograph operated by the master clock of the Bureau. The time of effusion for different intervals could, by this means, be determined to 0.05 second. Observational error in the timing was thus practically eliminated.

The apparatus shown in Fig. 3 was used when a lower effusion pressure and a larger volume was desired. The timing was either automatic, using terminals supported by the stopper, or the speed of effusion was observed by recording with a stopwatch the time of passage of the mercury column between the marks placed just below and above the main gas reservoir.

(*d*) **Orifices.**—Each orifice was made by piercing a small hole in a metal plate, and sealing it into a glass tube. All the orifice plates used for this investigation were of platinum-iridium (15 per cent iridium); this alloy makes a very stiff and serviceable plate. The orifice plate, usually 5 to 6 mm in diameter was pierced by a needle of appropriate size, using a soft metal backing. The hole was then cleaned out and enlarged as desired by proper reaming with a needle. Any burr could be removed and the plate ground down to the desired thickness by careful grinding on fine emery paper. When finished, the thickness of the plate was determined by means of micrometer calipers and the diameter of the orifice was determined with the aid of a microscope. The microscope was also used in determining the condition of the orifice during the finishing process. The plate, when completed, was sealed into the end of a glass tube and another glass tube sealed on next to it. The finished orifice then consisted of a platinum-iridium plate sealed into the center of a glass tube. After a little practice no difficulty was experienced in sealing the platinum plates into the glass so that they were mechanically strong and durable. The tubes were numbered by etching so that either face of the orifice plate could be identified at any time. The letters *A* and *B* are used to distinguish the two sides of the orifice. For example, when "orifice 10*A*" is used it means that orifice number 10 was used in such a position that the gas passed through the orifice from side *A* to side *B*.

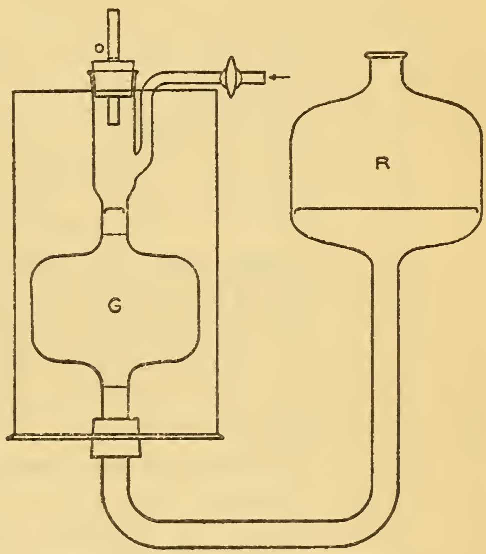

FIG. 3.—*Effusion apparatus for securing low pressures*

Orifice 22 was removed from its original tube after it had been in use for some time and was resealed in another glass tube; thereafter it was known as No. 22*X*. (See Fig. 5 and Table 3.)

5. EFFECT OF EXPERIMENTAL CONDITIONS UPON THE APPARENT SPECIFIC GRAVITY

The effect of variation of effusion pressure on the relative rates of effusion of air and hydrogen, argon, methane, and carbon dioxide through the same orifice (No. 28*B*) are shown by the curves in Fig. 4. The values of *R*, plotted as ordinates, are the ratios of the apparent specific gravities $\left(S=\frac{t_g^2}{t_a^2}\right)$ to the true specific gravity of the gas. The values of *r* plotted as abscissas are the ratios of the back pressure (atmospheric) to the effusion pressures. For example, if the atmospheric pressure is 760 mm of mercury and the average effusion pressure is 190 mm in excess of the pressure of the atmosphere, then $r=\frac{760}{760+190}=0.80$. The values of *r* nearest 1.0 represent the lowest effusion pressures.

A number of facts are at once evident from an examination of these curves. They illustrate in a striking manner the very different behavior of different gases. Different orifices give curves which have the same characteristic form for a given gas, although the values of *R* vary considerably. The apparent specific gravity is distinctly a function of the pressure. The combination of factors, which produces such a low result in the case of carbon dioxide, produces just the opposite effect in the case of hydrogen. While there may be a pressure at which the effusion method gives the correct specific gravity for a given gas with a given orifice, there is evidently no effusion pressure at which any one orifice will give the correct specific gravity for every gas.

Except for the correction due to the fact that the effusion is practically adiabatic, the major part of the deviations noted can be explained by differences in the viscosities of the gas and the air. If it were possible to calculate the correction in any given case, the fact that it would require a determination of the ratio of the specific heats, the viscosity, and possibly other physical constants of the gas, would prevent any commercial use of such a method. The theoretical consideration of these and similar curves will be left to a later paper, as previously stated. An empirical consideration of the facts will be used in this paper to demonstrate the most satisfactory conditions of operation for the method. The most important points to consider are the effusion pressure, the confining medium, and the orifice. Also of importance, but affecting

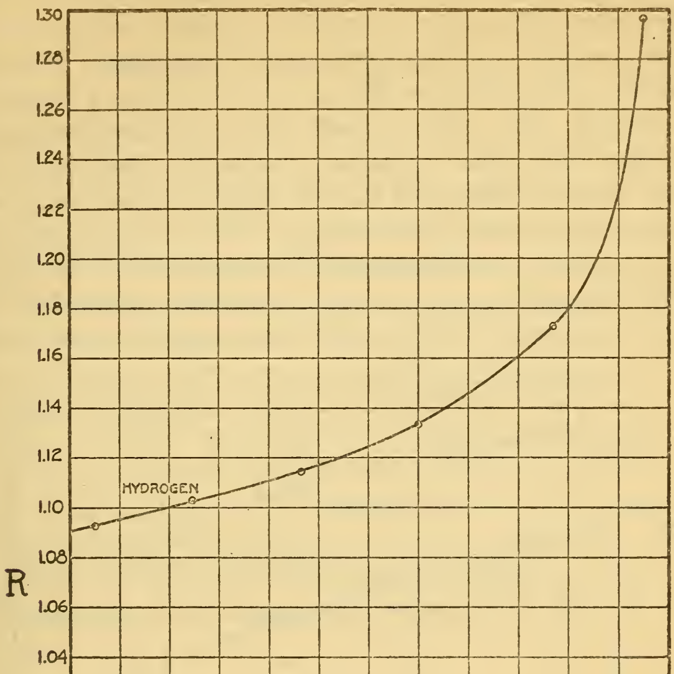

FIG. 4.—*Curves showing the apparent specific gravity of different gases as determined with orifice 28B at different effusion pressures*

only the accuracy and convenience of observation, are the shape of the apparatus and the method of timing.

(*a*) **Effusion Pressure.**—The effect of variations in the effusion pressure upon the relative rates of effusion of different gases was pointed out in connection with Fig. 4. When *r* equals 0.80 on the hydrogen curve, the apparent specific gravity is 10 per cent high; but when *r* equals 0.99, it is almost 30 per cent high. With carbon dioxide the calculated specific gravity is about 4.5 per cent low when *r* equals 0.80; but 15.5 per cent low when *r* equals 0.99. The largest deviations are seen to occur at the lowest effusion pressures (highest values of *r*), the deviations increasing rapidly between the values of *r* of 0.98 and 1. It may be concluded from these curves and a consideration of a large mass of other data that a very low effusion pressure should, in general, be avoided. However, the converse is not generally true, namely, that the higher

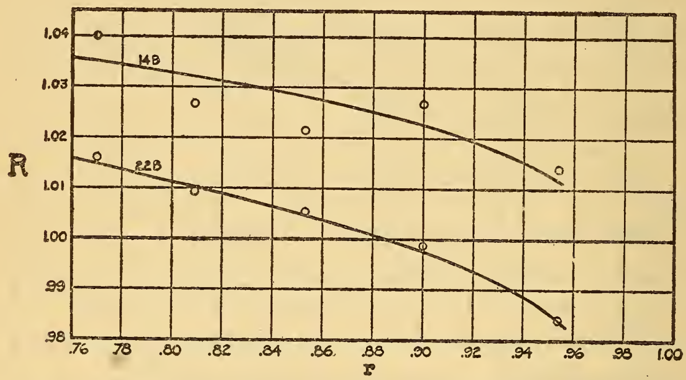

FIG. 5.—*Curves showing the apparent specific gravity of natural gas (specific gravity=0.748) using different orifices*

the effusion pressure the more nearly correct the apparent specific gravity will be, as is evident from the curve for the argon-air mixture in Fig. 4 and more strikingly from the two curves of Fig. 5. In connection with Fig. 5 it may be noted that the observed time intervals with orifice 14*B* were so small that the unavoidable errors of timing had a greater proportional effect than was the case for orifice 22, for example; this effect is seen in the greater deviation of the observed points from the most probable curve. It is evident that the character of the orifice as well as the gas under test must be taken into consideration in the choice of the effusion pressure.

(*b*) **Confining Medium.**—The question of the effusion pressure is closely connected with the choice of the confining medium, since the effusion pressure is partly dependent on the density of this medium. Mercury and water have been generally used for this purpose.

The use of water as a confining liquid is attended with a number of disadvantages. The gas, being in contact with water, must be measured saturated with water vapor at the temperature of the test; and the specific gravity value obtained is then the ratio of the weights of saturated gas and saturated air. The specific gravity of a gas is usually defined as the ratio of the weight of a given volume of gas to the weight of an equal volume of air, dry, free from carbon dioxide, and measured at the same temperature and pressure. This definition may be extended to include the value obtained with the effusion apparatus using water by stating that both gas and air shall be saturated with water vapor. It should be clearly borne in mind, however, that the specific gravity of dry gas referred to dry air may be very different from the specific gravity of saturated gas referred to saturated air. The latter value is, of course, not constant but is different at different temperatures and pressures. For example, if the specific gravity of a gas is 0.500, then the specific gravity of the saturated gas referred to saturated air at 20° C and 760 mm pressure will be 0.507. The development of the formulas by which this value is obtained is as follows:

Letting

S = specific gravity.

S_s = Specific gravity of saturated gas referred to saturated air.

d_w = density of water vapor $\left(\frac{d_w}{d_a} \text{ assumed to be } 0.622\right)$

d_g = density of gas (equals $S\ d_a$).

d_a = density of air.

p = pressure of gas and air.

p_w = partial pressure of water vapor at the temperature in question.

then

$$S = \frac{d_g}{d_a}$$

and

$$S_s = \frac{d_g(p - p_w) + d_w p_w}{d_a(p - p_w) + d_w p_w}$$

or rearranged

$$S = S_s - \frac{d_w p_w (1 - S_s)}{d_a(p - p_w)}$$

Since d_w, p_w, d_a, and p all depend on the conditions of temperature and pressure only, this may be put in the form $S = S_s(1 + k) - k$

or
$$S_s = \frac{(S + k)}{(1 + k)}$$

where
$$k = \frac{d_w p_w}{d_a(p - p_w)}$$

The values of k for different temperatures and at a pressure of 760 mm are given in Table 2. The effect of pressure may be neglected in the use of this table since changing the pressure from 760 mm to 730 mm changes k only from 0.0147 to 0.0153, a change which is negligible in most cases. To illustrate the use of the table: If the specific gravity of a gas is 0.660, then the specific gravity of the saturated gas referred to saturated air (S_s) at 25° will be $\frac{0.660 + .020}{1.0 + .020} = 0.667$.

TABLE 2

Values of K at 760 mm and Various Temperatures

$$k = \frac{d_w p_w}{d_a(p - p_w)}$$

Temperature	k
°C	
0	0.004
5	.005
10	.008
15	.011
20	.015
25	.020
30	.027

In the cases where the effusion apparatus was filled with water (Table 1) the term "specific gravity" is given the extended definition noted above. For the small range of temperature in which the experiments were made the specific gravity was nearly constant, the variation not being significant in comparison with the errors of the determination.

The expansion of the gas in passing through the orifice results in a considerable lowering of its temperature with the consequent condensation of water vapor. This water frequently adheres to the rim of the orifice, materially changing its diameter and giving erroneous results for the apparent specific gravity since the area of the orifice may vary from one test to the next as water is condensed or evaporated from its walls. When this occurs the effusion time may vary quite erratically. Condensation of water vapor is undoubtedly responsible for the changes observed in the effusion time in the following consecutive series of readings with air: 149.6 (seconds), 152.2, 153.0, 155.8, 157.8, 157.6, 157.8, 158.4, 159.0. The orifice was removed and dry air passed through and another series of readings with moist air taken as follows: 151.0, 153.4, 155.4, 156.0. No difficulty was experienced in securing constant readings when using dry air.

The gradual increase in effusion time was evidently caused in each series by the gradual obstruction of the orifice by the condensed water. Drying the orifice reduced the time practically to its original value for the first test of the second series. When this difficulty was experienced, passing dry gas through the orifice previous to each test made it possible to secure consistent readings, thus confirming the belief that the condensation of water vapor was the cause of the erratic results. The remarkable feature is that the difficulties caused by the water vapor are not more serious.

The solubility of gases in water may also be a source of error when using water

Mercury is the ideal confining medium from the standpoint of precision, since its vapor pressure is negligible and gases are insoluble in it. Its high density may, however, introduce difficulties when it is desired to secure a low effusion pressure. Mercury was used in most of the experiments reported. However, in a few cases (Table 3*b*), when it was desired to secure results at low pressures, concentrated sulphuric acid was used in its place, because of its low density and also because of its low vapor pressure. Except for experimental purposes, however, sulphuric acid is not recommended, because of the inconvenience and liability of accidents occurring in its use.

An oil of some kind might be used when it was desired to secure a liquid of low density and low vapor pressure. The appreciable solubility ot natural gas, for example, in paraffin oils is, however, a very undesirable feature. The viscosity of the oil, unless very low, might also introduce errors.

(*c*) **Orifice.**—The character of the orifice employed is of prime importance. This is apparent from the fact that different orifices when used under the same conditions give widely varying results; the same orifice will also give different results when certain of the operating conditions are varied. In order, therefore, to make an intelligent selection of orifices it is necessary to know, at least qualitatively, the effect of varying the shape, size, etc., of the orifice.

The shape of the orifice has an important effect upon the relative rates of effusion. The same orifice used under exactly the same conditions except that the direction of flow through it is changed, may give a different apparent specific gravity, thus showing the effect of changing the form of the orifice (as viewed from the side of the effusing gas) without changing its diameter. In Fig. 6, for example, the curves for orifices 25*A* and 25*B* show that reversing

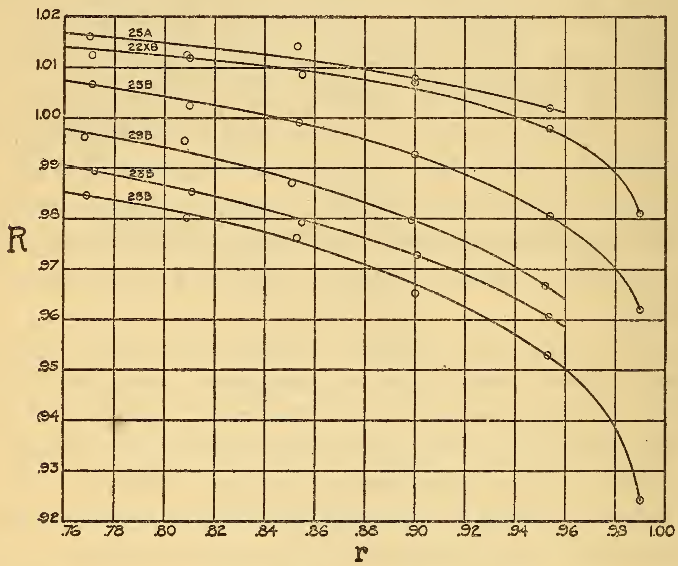

FIG. 6.—*Curves showing the apparent specific gravity of "methane" (specific gravity=0.583) using different orifices*

the orifice in the apparatus makes a difference of 1 to 2 per cent in the apparent specific gravity. An examination of the results given in Table 3 shows differences as large as 2.3 per cent between the two sides of an orifice, and much greater differences have been noted for other orifices, especially in the case of certain ones with ragged edges. Of course, the more nearly alike is the form of the two sides, the closer will be the agreement secured with them; but differences so small as not to be apparent, even under considerable magnification, may produce a noticeable effect. The form of the edges of the orifice on the inner side of the plate determines largely the line of flow of the gas into the orifice; it may also change the effect due to the viscosity of the gas.

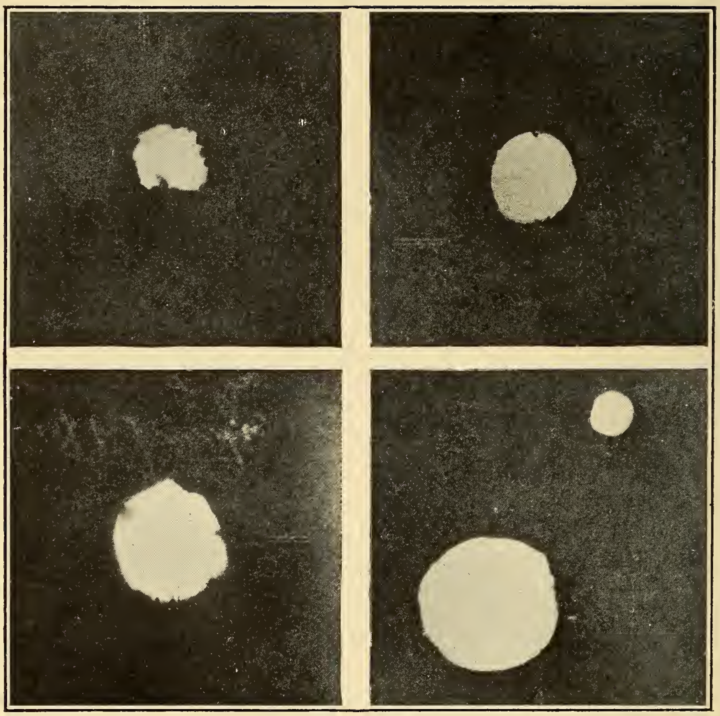

FIG. 7.—*Photomicrographs of four orifices used with the apparatus shown in Fig. 1*

The orifice may vary in shape from a cylinder to a cone, with either sharp or ragged edges, or rounded off in many different ways. When the orifice is made simply by punching a hole in a metal plate without removing the bur, an irregular shaped orifice may be produced, the rough edges of which are very likely to catch dust particles. Fig. 7 shows photomicrographs of four orifices[4] some of which were used in the preliminary tests. These orifices were evidently made by punching the orifice plate after it had been sealed in the end of the glass tube and the bur was on the inner side of the plate. The appearance of such an orifice, somewhat enlarged, is shown in Fig. 8*a* and *b*. It seems probable that the orifice used in position *a* is practically equivalent to the sharp-edged orifice shown in Fig. 8*c*. Rounding off of the edges of the latter tends to produce an orifice similar to *b*, although seldom so pronounced.

The orifices made by punching without removing the bur usually gave higher results with natural gas when used in position *a* than when reversed to position *b;* and a shorter effusion time was always observed when the orifice was used in position *b*. For example, orifice No. 1 used in position *a* in an apparatus like that of Fig. 1 (normal position in this case) gave a value 1 per cent high; when reversed it gave a value 7.5 per cent low. The time of effusion for air in the first position was 90 seconds and in the second position 78 seconds.

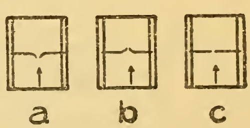

Fig. 8.—*Characteristic orifice shapes*

The experimental results show that, almost without exception with the orifices examined, the position showing the lower air effusion time gives for the natural gas the lower value for the apparent specific gravity. The same factors would have the opposite effect in the case of hydrogen, giving a higher apparent specific gravity. Some idea of the character of an orifice may be obtained by comparing the air effusion times when it is used in both positions. If there is considerable difference, the position giving the longer time is the preferable one to use.

There seems to be no advantage in the use of an orifice like Fig. 8*a* and *b*, but if it is so made it should be used in position *a*.

It was practically impossible to control the exact form when making such small orifices. Except in a few cases, the orifices made for this investigation had the bur carefully removed and the

[4] See Table 1.

orifice was made as nearly cylindrical as could be done with a needle; the edges of the orifice were unavoidably slightly rounded in many cases, however. Of the orifices mentioned in the succeeding paragraphs of this section, all except orifice No. 16, had had the bur removed. A series of orifices of this character, varying in size and thickness of plate, was made and tested.

The variation in the apparent specific gravity of methane when determined with six different orifices is shown in Fig. 6. It is to be noted that in form the curves are quite similar. The characteristics of these orifices were as follows:

Orifice	Diameter	Thickness of plate
	mm	mm
25	0.12	0.09
22	.09	.02
29	.05	.05
23	.07	.04
28	.07	.10

Similar series of curves have been obtained for the other gases used. The results are in each case a set of nearly parallel curves, with the same relative arrangement with respect to the orifices. With curves shaped like those for carbon dioxide or methane in Fig. 4 the larger orifice gives the higher result, but with curves like those for hydrogen and argon the larger orifice gives the lower values.

These with other results show that, in general, an increase in the thickness of the plate or decrease in the diameter of the orifice results in a lower apparent specific gravity for the methane. In the case of hydrogen the converse is true, the same changes producing an increase in the apparent specific gravity. (See Fig. 4.)

A more definite idea of the effect of size of orifice can be obtained from a consideration of the data in Table 3, where results for methane with fourteen different orifices are recorded. The time of effusion of the air (190 cc) is included for purposes of comparison.

TABLE 3

Effect of Size of Orifice

(*a*) Tests made with mean pressure ratio (r) of 0.92 using methane of specific gravity 0.583

Orifice	Diameter of orifice	Thickness of orifice plate	Time of effusion for air	Apparent specific gravity	Error
	mm	mm	Sec.		Per cent
22 x A	0.09	0.02	587	0.580	−0.5
22 x B	.09	.02	608	.589	+1.0
21 A	.18	.02	107	.588	+0.9
21 B	.18	.02	107	.590	+1.2
19 A	.25	.02	57	.588	+0.9
19 B	.25	.02	57	.589	+1.0
14 A	.14	.04	160	.575	−1.4
14 B	.14	.04	170	.588	+0.9
16 A	.20	.04	75	.577	−1.0
16 B	.20	.04	84	.585	+0.3
18 A	.19	.06	98	.576	−1.2
18 B	.19	.06	103	.586	+0.5
7 A	.14	.07	145	.582	−0.2
6 A	.19	.07	86	.585	+0.3
8 A	.22	.07	68	.583	0.0

(*b*) Tests made with mean pressure ratio (r) of 0.99

Orifice	Diameter of orifice	Thickness of orifice plate	Time of effusion for air	Apparent specific gravity	Error
22 x A	0.09	0.02	1034	0.572	−1.9
22 x B	.09	.02	1045	.572	−1.9
21 A	.18	.02	260	.583	0.0
21 B	.18	.02	261	.583	0.0
19 A	.25	.02	134	.586	+0.5
19 B	.25	.02	133	.589	+1.0
30 A [a]	.37	.03	66	.599	+2.7
30 B [a]	.37	.03	65	.598	+2.6
26 A	.15	.04	356	.572	−1.9
26 B	.15	.04	346	.566	−2.9
18 A	.19	.06	249	.571	−2.1
18 B	.19	.06	254	.574	−1.5
27 A	.25	.05	120	.585	+0.3
27 B	.25	.05	120	.584	+0.2
28 B	.07	.10	1772	.539	−7.5
25 A	.12	.09	544	.569	−2.4
25 B	.12	.09	549	.560	−3.9
24 A	.18	.09	255	.579	−0.7
24 B	.18	.09	244	.571	−2.1

[a] The results obtained with orifice No. 30 may be somewhat high owing to the fact that the viscosity of the sulphuric acid used as a confining medium in this test may have slightly retarded the rapid flow of the gas.

The relative times for the effusion of a given volume of air with different orifices give some idea of their relative sizes, particularly when the differences in time are large. Considerable caution should be used, however, in taking the effusion times as a criterion of relative size, because of the large effect that the shape of the orifice has on the absolute rate of effusion.

6. RECOMMENDATIONS

(*a*) **Types of Apparatus.**—The two general groups of apparatus in use may be called the displacement type and the expansion type, respectively. In the first class may be placed those instruments in which one observes the time of effusion of a definite volume of gas actually displaced by the confining liquid. In the expansion type class may be placed those instruments in which one observes the time required for the effusion of the gas which escapes during the expansion from high to low pressure, the volume remaining practically constant. The apparatus shown in Figs. 1, 2, and 3 are typical of the first class, the space occupied by the effusing gas being filled by the rising column of the confining medium. In Fig. 9 is shown an apparatus of the second type where the driving pressure is obtained almost wholly from the expansion of the effusing gas. In this apparatus the time observed is that required for the pressure in the gas chamber (*G*) to fall a certain amount, as shown by the manometer (*M*). The principal advantage of apparatus of the expansion type lies in the small quantity of confining liquid necessary, which is important where mercury is being used. In this type the volume of mercury necessary for the manometer can be made very small.

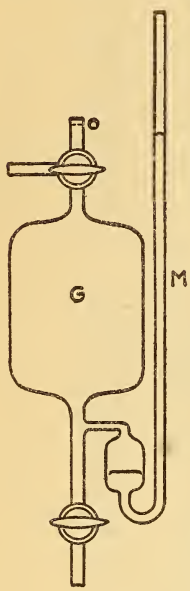

FIG. 9.—*Expansion type of effusion apparatus*

It amounts to the same thing whether one determines loss in pressure or change in volume, but the relations between the volume of the gas chamber, the effusion time, and the effusion pressures are very different for the two types of apparatus. To secure the same effusion time with apparatus of the expansion type as with the displacement apparatus it is necessary that either the volume of the apparatus or the effusion pressure be considerably increased. For example, if an apparatus of each form has a gas reservoir holding 100 cc, and if the pressure at the start of a test is 1/10 atmosphere above atmospheric and the pressure at the finish is that of the atmosphere, then using the same orifice on each apparatus, the time of effusion will be approximately eleven times as long with the apparatus of the displacement type as with the expansion type. To give the same time of effusion would require a total volume in the expansion apparatus of about eleven times that in the displacement type of apparatus. An interval long enough for accurate timing must be obtained, and since increasing the time of effusion by decreasing the size of the orifice is permissible only within certain limits, it may readily be seen that an apparatus of the expansion type with an orifice of the proper size might have to be very large and cumbersome in form; this type of apparatus is not recommended.

The relative advantages in the use of water or mercury as a confining medium have been discussed in a previous section and the choice should be made according to the requirements of the user. Two forms of apparatus are suggested in the following paragraphs, the first suitable for use with either mercury or water as a confining medium and the second, a somewhat simplified form, suitable for use with water only. There is nothing essentially new in this apparatus; it is a combination of the most desirable features which have been suggested.

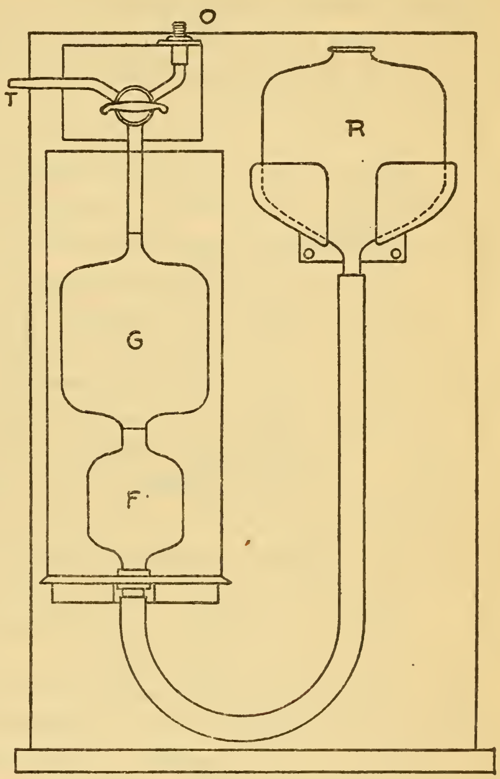

FIG. 10.—*Form of apparatus recommended for use with mercury or water*

(*b*) Forms of Apparatus of Displacement Type.—The form of apparatus shown in Fig. 10, while especially adapted for use with mercury, is equally suitable for use with water if a few minor changes are made, so that the effusion pressure is adjusted to a suitable value. The gas chamber (*G*) should be made spherical or cylindrical in form, as shown, and should have a capacity of about 150 to 200 cc. This shortened form of gas chamber gives the necessary gas capacity without at the same time increasing the effusion pressure beyond suitable working limits with mercury, as might easily be the case if a cylindrical chamber similar to that shown in Figs. 1 and 2 were used.

The smaller cylinder (F) is provided so that when the sample is drawn in at atmospheric pressure, there will be sufficient gas capacity to permit the compression of the gas caused by raising the reservoir (R) to its position and yet leave the mercury a suitable distance below the lower graduation. If water only is to be used in the apparatus, this extra capacity can be reduced accordingly.

The gas chamber is connected to the reservoir (R) by means of a rubber tube and to the orifice tube (O) by the glass tube and stopcock, as shown. The gas chamber is water jacketed to maintain a uniform temperature.

Reference marks are placed on the tubes just above and below the gas chamber and the time of effusion is determined by observing the interval required for the meniscus to pass between these two marks. The accuracy with which the position of the meniscus can be observed varies with the diameter of the tube and the speed with which the meniscus is moving. With the apparatus of Fig. 1 some difficulty is experienced on this account because of the uncertainty as to just when the moving meniscus is on the mark. The eye can be aided by various devices, but the accuracy of reading is materially improved by the use of smaller tubes as here recommended. The diameter of the tubes at the top and bottom can be so proportioned that the speed of the meniscus is approximately the same both at the start and finish of a run. Making the upper tube small has the further advantage of reducing the gas space between the liquid and the orifice, which must be swept out when introducing the gas sample.

Attached to the upper tube is a three-way stopcock by means of which the gas chamber may be connected either to the side tube (T) for filling or to the orifice which is attached at O. This stopcock also may be set so that gas can be passed through the orifice from the inlet (T) while the gas chamber is closed off. This makes it possible to sweep out the orifice tube and connections and eliminates the uncertainty connected with the use of the apparatus shown in Fig. 1, where the space between the stopcock and the orifice is left filled with a mixture of gas and air which one must assume is swept out by the time observations are commenced. When using water with this apparatus any moisture condensed in the orifice can be removed by passing dry gas or air from this side tube through the orifice; this will be found to be the most convenient and satisfactory way of drying the orifice.

The orifice tube (see Fig. 12) screws onto the small metal support at O, into the base of which is cemented the glass tube leading from the stopcock. Suitable supports for the stopcock and the water jacket are required to hold the parts in position and to prevent breakage.

The reservoir *R* is supported at a fixed height by a holder and is connected to the gas chamber by a large heavy-walled rubber tube, securely fastened in place. By raising or lowering the bulb, gas or air can be forced out or drawn into the gas chamber; but it is essential that the support be so shaped that the reservoir will be always at exactly the same height relative to the gas chamber so that the effusion pressure is maintained constant. Another support for the reservoir at a lower level is convenient when filling the apparatus with gas.

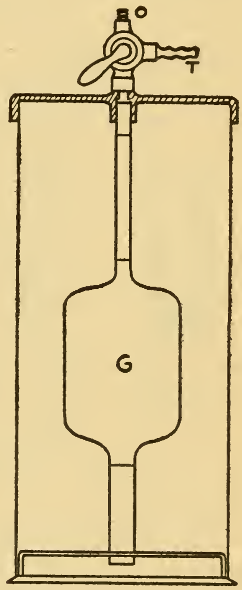

FIG. 11.—*Simplified form of apparatus for use with water only*

The apparatus should operate with an effusion pressure of 15 to 20 cm of mercury at the start of a test and 1 or 2 cm at the finish; this gives a mean pressure ratio *r* of about 0.90. If water is being used the pressure should not be reduced below 5 cm of water at the finish of a test. The length of the tube between the upper mark and the stopcock should be adequate to permit this, if it is intended to use water.

In Fig. 11 is shown a simplified form of apparatus for use with water, which may have certain advantages in some cases. The tube at the bottom of the gas reservoir is open and is kept centered by a small metal ring. The tube at the top is cemented into a metal cover resting on the edge of the jar. Attached to this cover is a metal stopcock, which may be made just like that shown in Fig. 10, or it may be a T-bore cock, as shown in Fig. 11. In any case, the tap of the stopcock should have a circumference sufficiently large relative to the size of the openings that the various openings can be made to register properly without the use of excessive care in setting. The use of reference marks on the tap and barrel will also aid materially in rapid and accurate setting of the cock. Gas and air can be introduced into the gas chamber, providing their pressure is sufficient; otherwise it is necessary to make the cover detachable and partly lift the gas chamber out of the jar in order to fill it with the gas or air.

The tube connecting the gas chamber with the stopcock should be about 6 mm internal diameter and at least 10 cm in length above the upper graduation. The lower tube should be about 15 mm internal diameter and at least 8 cm long below the lower graduation.

(*c*) **Orifice.**—A desirable form of orifice is shown in Fig. 12. The orifice plate, of the form described below, is sealed into the center of a short glass tube, 3 to 6 mm internal diameter. This tube is mounted with khotinsky cement in a metal casing, threaded at the end so that it can be attached to the apparatus. The orifice is thus protected from breakage and it can be readily removed for examination or cleaning. Constrictions in the orifice tube or connections do not influence the results unless they are very long or small in diameter.

As a guide to the selection of the proper size of orifice, the following general recommendations are made. It should be clearly recognized from the previous discussion of this subject that no definite limits of size can be set, but it is believed that the following specifications will aid materially in the construction of a satisfactory orifice.

Fig. 12.—*Form of orifice recommended*

For apparatus designed to operate with a mean effusion pressure ratio of 0.90 (Fig. 10, used with mercury) an orifice plate 0.05 mm or less in thickness and having a smooth cylindrical orifice between 0.15 mm and 0.30 mm in diameter should prove best adapted for this purpose.

For apparatus designed to operate with a mean effusion pressure ratio of 0.99 (almost any apparatus using water) an orifice plate less than 0.04 mm in thickness and having an orifice between 0.18 mm and 0.30 mm in diameter should be chosen.

In the above specifications an upper limit is set for the thickness of plate; the lower limit is determined by the strength of the material. The upper limit for the diameter is largely determined by the time of effusion which is considered necessary in order to give the desired precision in the timing. Too large an orifice is, therefore, to be avoided, as well as one too small. The diameter of orifice as recommended in some text books is undoubtedly too small.

(*d*) **Standardization.**—In control work or where only comparative values are desired on gases of the same general nature, considerable reliance may be placed in the effusion method. It is evident, however, that where the absolute specific gravity of the gas must be known, little or no reliance can be placed in results obtained with an apparatus the operating characteristics of which are unknown. Whenever possible it is recommended that a preliminary standardization of the orifice be made. To be significant, it is essential that any standardization be made using a gas of the same character as that to be tested and whose specific gravity has been determined with the necessary accuracy by an independent method. The specific gravity balance for gases described in Technologic Paper No. 89 of this Bureau furnishes a suitable means of determining the specific gravity for this purpose. Such an empirical standardization will not only give the magnitude of the errors occurring, but may also be used to determine an approximate correction for the observed values with a consequent gain in precision.

The results shown in Table 1 were thus used to obtain correction factors for the orifices tested with the idea of increasing the precision obtained with them until the method had been more thoroughly investigated. This was practicable since these orifices were being used only with natural gases of the same general character as that employed for the preliminary test. An empirical factor was decided upon which should represent the average amount to be added to the apparent specific gravity to give the correct value; the correction factors recommended for use were for orifices No. 4, −0.010; No. 12, +0.005; and No. 11, +0.020. For example, if the apparent specific gravity of a sample of natural gas was found to be 0.661 using orifice No. 4, the corrected value would be 0.651. Where the correction for an orifice was as large as 0.030 it was recommended that the use of the orifice be discontinued because of the uncertainty in the application of such a large empirical correction. Considerable success was attained in the use of these correction factors in field tests as indicated by the agreement between the corrected values. Table 4 shows the results of a number of these tests made by H. T. Ashton and T. A. Kerr. The use of the correction factor reduced the average difference between results obtained with the use of orifices Nos. 4 and 11 from 5 per cent to less than 1 per cent. Usually a fair agreement was secured between the corrected results with orifices Nos. 11 and 12; those reported are representative of the worst obtained. Such irregularity is to be expected, when one considers the sources of error possible in the water-filled apparatus and the nature of the empirical correction. Undoubtedly greater precision can be obtained with the use of dry gas, since the errors due to condensation in the orifice are obviated and the specific gravity is not a function of the temperature and pressure.

TABLE 4

Field Tests Showing Use of Correction Factor

Gas [a]	Apparent specific gravity			Corrected specific gravity		
	Orifice 4	Orifice 12	Orifice 11	Orifice 4	Orifice 12	Orifice 11
A	0.661	....	0.633	0.651	....	0.653
B	.668	....	.635	.658	....	.655
C	.681	....	.647	.671	....	.667
D	.691	....	.661	.681	....	.681
E	.687	0.674	.648	.677	0.679	.668
F	.683	.682	.644	.673	.687	.664
G	....	.660	.652	....	.665	.672
H	....	.679	.666	....	.684	.686
I	....	.648	.643	....	.653	.663
J	....	.660	.635	....	.665	.655

[a] Gas J was the same as gas I except that the test labeled I was made at the measuring station and test J was made on a sample taken to the laboratory.

(*e*) **Operating Directions.**—In the preceding sections of this paper most of the details of operation of the apparatus have been discussed; only a short summary of the operating directions together with certain precautions to be observed will be given here.

The apparatus should be set up and filled with the confining liquid to the proper level; a mark may be placed upon the upper tube at the proper height to aid in reproducing this level.

In filling the apparatus with gas or air, care should be taken to insure an uncontaminated sample by rinsing as many times as may be necessary to obtain constant effusion times in successive tests. The orifice tube and connections must also be filled with the gas sample.

When using a movable reservoir as shown in Fig. 10, care should be taken to replace the reservoir at exactly the same height, so that the effusion pressure will not be changed from one determination to the next.

The apparatus should be tested to make sure that there are no leaks in the gas chamber.

Any moisture condensed on the edges of the orifice should be removed by passing dry gas through the orifice. The constancy of the air effusion interval is an indication of whether or not an appreciable error is being introduced from this source.

For a specific gravity determination, several consecutive runs should be made on both gas and air. In general, one should secure three or four intervals which agree within 0.5 per cent, or if the interval be more than two minutes, within one-half second, before the average can be considered as satisfactory. It should be noted that an error of 0.5 per cent in timing makes a difference of about 1 per cent in the apparent specific gravity. The accuracy of the stop watch should be checked by comparison with some standard when possible.

In timing, care should be taken to have the eye on a level with the graduation at the time of starting or stopping the stop watch.

7. SUMMARY.

The effusion method of determining gas density, which is based upon the fact that the times required for the escape of equal volumes of two gases under the same pressure through the same small orifice are approximately proportional to the square roots of the densities of the gases, was investigated in order to determine the accuracy of the method and its sources of error. In cooperation with a number of men employing this method in the natural-gas industry, a series of experiments was made, using their apparatus under field conditions. It was found that results in error by more than 10 per cent were not unusual.

The theory of the effusion process was investigated in order to determine the influence of the numerous variables affecting the apparent specific gravity. The relative rates of effusion of air as compared with hydrogen, argon, methane, and carbon dioxide at different pressures and with different orifices were determined. A more detailed treatment of the theory in the light of these results will be given in another paper. The results obtained from this study, together with the observations made on the effect of the effusion pressure, the confining medium, and the shape and size of the orifice were used in determining the most favorable conditions of operation for this method. Recommendations are made as to the most suitable type and form of apparatus for use and specifications given to guide in the construction of the orifice.

Although no results of high accuracy can be expected from apparatus of the effusion type, yet it should serve well for approximate results or for work where relative values only are needed, as in control work.

It has been shown that the apparent specific gravity as determined by this method can be varied within rather wide limits by changing the conditions. However, by the observance of certain precautions in the construction and use of the apparatus, it is

possible to secure results accurate to about 2 per cent. The greatest precision is obtained where the physical properties of the gas tested show the least difference from those of air. Some further increase in accuracy, and particularly in reliability, can be gained by standardizing the apparatus as recommended.

Where a more accurate method is desired, the specific gravity balance for gases described in Technologic Paper No. 89 of this Bureau may be used.

WASHINGTON, February 5, 1917.