METHODS of DETERMINING

the

SPECIFIC GRAVITY of GAS

by

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INTRODUCTION

In all fields of the gas industry, we find that specific gravity is one of the most common tests made on the gas. Though this property does not always vary with a variation in the constituents of the gas, a variation of the specific gravity will usually mean a variation in the percent of the constituents and a quick and accurate method of obtaining specific gravity is very serviceable in the gas industry at times. Perhaps the most important use of the gravity of gas is in the measurement of gas volumes by means of the orifice and flow meters. In measuring the volumes of gas by means of the Orifice Meter[1] for instance, the formulas are calculated for a certain specific gravity 0.6 or 1.0 and for any variation in gravity a correction must be made. An error of one to two percent in the determination of the gravity of the gas, which is not at all uncommon in ordinary practice, will result in an error of 0.5 to 1.0% in the corrected volume of gas measured. One can readily see that under such conditions the errors will soon mount up into large sums of money in the transfer of large volumes of gas. Gasoline content is adso sometimes estimated from the specific gravity though this is a somewhat ~~inacurate~~ inaccurate method. In the illuminating gas industry certain of the constituents, oxygen and carbon dioxide content are often determined from the specific gravity. The Lux[2] balance is a type of apparatus used in this connection and is often graduated to read in percent of the constituent desired instead of specific gravity. It can readily be seen from

1. Bul. Supplement #111 G. Metric Metal Works, Erie, Pa.
2. Technical Gas Analysis by Lunge, P. 183.

this brief review that specific gravity is quite often of great importance in the gas industry. It is evident, however, that any method of determination should combine ease of manipulation with rapidity and accuracy. The different methods commonly used vary considerably in accuracy and the importance of the test and accuracy desired will therefore govern the method that should be used. The effusion method, because of its rapidity and ease of manipulation, is the one most commonly used in the gas industry. There are many sources of error in the method, but its accuracy is surprising when due precautions are taken. It is the purpose of this thesis to give a comparison of the different methods of determining specific gravity of gas and also to give their merits and demerits. It is also the purpose of the thesis to investigate the errors of the effusion method and explain how they may be corrected. Though under certain conditions the method is quite inaccurate, it is by no means to be discarded but rather to be so manipulated as to eliminate the inaccuracies.

DIFFERENT METHODS EMPLOYED TO DETERMINE THE SPECIFIC GRAVITY OF GASES

There are four principal methods by which the gravity of a gas may be determined: the effusion method; gas density balance method; direct weighing method and by calculation from the analysis. Below is given an outline of some of the different methods used. Other methods are a modification of one or more of the various types.

The effusion method was first used by Bunsen and the different types are but modifications of his method. The method is based upon the fact that the specific gravities of two gases escaping through an orifice or narrow opening in a thin plate have nearly the same ratio to each other as the spuare of their speeds of escape.

For example:

$$\frac{S_1}{S_2} = \frac{t_1^2}{t_2^2}$$

; where gas S_1 has a speed of escape t_1 and gas S_2 has a speed of escape t_2. Air is usually run as S_2 and regarded as 1.0 so that the equation becomes $S = \dfrac{t_1^2}{t_2^2}$.

The type of apparatus used by Bunsen[1] consisted of a glass tube about 70 cc. capacity luted into an iron cap which was fitted with a three way stop cock by means of which the glass tube could be brought into communication with the tube through which the gases were introduced, or a small opening in a platinum plate at the top of the apparatus. A float was placed inside the tube and the open end of the tube set in a cup of mercury. In making a run the tube containing the gas was pushed down into the mercury so that the float was no longer visible above the outer surface of the mercury. The float was marked at the top and neat the bottom and

1. Hempel Gas Analysis; Translation by L. M. Dennis, P. 269.

by observing it through a telescope the time of escape was taken for the volume of gas in the tube, represented by the distance between the two marks.

J. A. Butterfield[1] in his work on the chemistry of Gas Manufacture gives the apparatus a slightly different form.

Schilling[2] apparatus is a modification of that used by Bunsen and is made in several slightly varying types. One type consists of a glass jar about 3½ inches in diameter and about 12 inches deep, into which is inserted a glass tube 1 inch in diameter, graduated each inch from the bottom upward. The later type has a constriction in the tube at the graduation so as to reduce the error in reading. The tube is mounted on a brass plate at the top of the jar, through which it is inserted, and attached to it are a three-way stop cock and a small glass tip with platinum orifice plate fused across its upper end.

The test is made by filling the jar with water almost to the top, inserting the graduated tube with the cock open to allow the water to enter. The tube is now filled with air by withdrawing it with the tip removed and the cock open. It is reinserted with the cock closed and the tip replaced. The cock key is then turned to permit the air to escape through the orifice tip, being forced out by pressure of the water rising in the tube from the jar. The time of effusion for air is then found by taking the time required for the water to rise between two of the graduations on the inner tube and the time for gas found in the same manner. Calculations are made as with the Bunsen method.

1. American Gas Engineering Practice; Latta P. 281.
2. American Gas Engineering Practice; Latta :. 283.

The method[1] as modified by the Bureau of Standards has a constriction on each side of the bulb, for the points where the readings are taken, and a leveling bulb attached. The purpose of the bulb is to have less difference in water level through extending the body laterally, thereby giving a more satisfactory effusion pressure.

The Jenkins[2] specific gravity apparatus varies slightly from the Schilling in that the effusion tube is connected directly to a leveling tube device which can be set at the desired level to furnish a water head. A curved piece of brass wire pointed at the end serves for the bottom marker and a scratch on the glass serves for the top marker. The orifice is made in a thin platinum plate as with the other methods.

The Lux[3] specific gravity balance has been used to considerable extent in gas works. The apparatus is made on the principle of the common lever balance. The gas is introduced ~~to~~ into the globe of the balance which is suspended on pivots, the gas ways being sealed by mercury cups, and passes away to a convenient service. The balance being adjusted, the specific gravity (uncorrected for temperature, atmospheric pressure, and aqueous vapor) is indicated by a pointer and read direct on the scale. The scale is previously calibrated by weighing air in the globe under standard conditions and calling the indicated point 1, and then weighing hydrogen under the same conditions and calling the point .07. Correction factors are used for variations in temperature and pressure.

The Edwards[4] gas density balance has been designed by the Bureau

1. Technologic Paper No. 94 of the Bureau of Standards.
2. Practical Testing of Gas and Gas Meters; Stone, P. 262.
3. Abady Gas Analyst's Manual, P. 167.
4. Technical Papers No. 89 of the Bureau of Standards.

of Standards and they recommend its use for determining gas densities. It consists of a balanced beam having a sealed globe on one end and a counter weight on the other. The beam with its support is mounted in a gas tight chamber to which is attached a mercury manometer. The balance is provided with a scale so that the beam can be balanced with dry air and then with dry gas at some certain point. The pressure indicated by the manometer is read and recorded. The gravity of the gas is inversely proportional to the absolute pressure.

A very unique type of density balance is that devised by Aston in his experiments on Neon[1]. The balance described is a microbalance and is devised for use with minimum quantity of gas (about 1 cc.). The balance is constructed on the same principle as the Edwards gas density balance, the sensitivity of the balance being 10^{-6} mgrm., and affords an accuracy of 0.1 percent.

The most standard way of determining the gravity of gases is the direct weighing method. The usual procedure is to weigh a flask, using a similar flask as a counterpoise, containing dry air and then weigh the flask filled with dry gas. Dr. Letheby[2] devised a special glass globe for this method. The globe had extensions and valves above and below and the upper end terminated by a tube containing a sensitive thermometer. With temperature and pressure constant, the gravities of gases are proportional to the weights of equal volumes. The methods used by Regnoult and Bunsen[3] are among the first standard methods described for determining the gravity by this method.

1. Handbook of American Gas Engineering Practice. Latta.
2. Watt's Dictionary of Chemistry.
3. Hamor and Padgett, Examination of Petrolum.

The gravity of gases can also be obtained by calculation[1] from chemical analysis. Calculation from the analysis is made as shown in one of the following paragraphs. The accuracy of the method depends entirely upon the accuracy of the analysis and since considerable skill and technique are required for analysing gases, this method of obtaining specific gravity is not advisable unless the analysis is made by an experienced analyst.

The Jet photometer[2] which has been used to a small extent to determine the gravity of gases affords only an approximate and inaccurate method and has fallen into disuse.

1. Proceedings Royal Society, A 89, P. 439; 1914.
2. Stone - Practical Testing of Gas and Gas Meters. P. 265.

A COMPARISON OF THE DIFFERENT METHODS OF DETERMINING SPECIFIC GRAVITIES OF GASES.

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A comparison is here made of the four principal methods just discussed; the Effusion method, Gas Density Balance Method, Calculation from the analysis Method and the Direct Weighing Method. The procedure that was followed for the different methods is given below.

DEFINITION OF SPECIFIC GRAVITY AND DENSITY

Before giving a comparison of the methods mentioned, the terms specific gravity and density will be defined as they are to be used in this work.

The density of a substance is defined as the mass divided by the volume and is usually given as the weight in grams of one cubic centimeter of the substance. The temperature and pressure must therefore be specified since the mass per unit volume will vary with a variation of these conditions due to the contraction or expansion of the substance. Density, then, by definition, is an abstract term and this definition applies to the term as used throughout the work.

Specific Gravity is defined as the ratio of the density of a substance to the density of another substance taken as an arbitrary standard. The standard ordinarily used in gas work is air, the specific gravity being taken as one. The specific gravity of a gas therefore, unlike the density, will not necessarily vary with a variation of temperature or pressure if the comparison is made under like conditions. In the case of gases which show deviations from Boyle's Law or of gases which do not show the same degree of deviation as air, the specific gravity will vary from the true gravity at those temperatures and pressures, where deviation from Boyle's Law are shown. For ordinary temperatures and pressures, however, the deviation of most gases is so small that the variations shown are inappreciable except in very accurate work. The definition as given above applies to gases in a dry state. With the Effusion Method water is practically always used as the confining liquid in determining the gravity of gases so that the specific gravity is given in terms of the gas saturated with water vapor. This value is therefore termed apparent specific gravity and must be corrected for water vapor as shown on page 35 to obtain the (true) specific gravity.

EFFUSION METHOD.

The method used was the same as that most commonly used in commercial practice. The type of apparatus used and procedure followed is given in detail on page 30. Water was used as the confining liquid and some error was therefore introduced, due to the air and gas being saturated with water vapor. Quite a large number of determinations were made with the particular apparatus used and it always gave satisfactory and consistent results. The correction for water vapor was the only correction which needed to be applied to the results obtained. This source of error is discussed in more detail on page 32, and a correction formula is also given. Data from a typical run is given below.

	Time for air Seconds	Time for gas Seconds
	101.0	77.0
	101.0	77.0
	101.0	77.0
	100.8	77.0
	100.8	77.0
Average	100.9	77.0

Specific gravity of gas (Saturated with water vapor) ....

$$\frac{(77.0)^2}{(100.9)^2} \triangleq .584$$

Temperature of Experiment = 25° C.

Specific gravity of gas (Corrected for water vapor)

$$S = .584 (1 + .02) - .02 = .575$$

GAS DENSITY BALANCE METHOD

The Laboratory type of Edwards Gas Density Balance was used for determining specific gravity by this method. Technologic Paper #89 of the Bureau of Standards gives quite a detailed description of the apparatus and method. Although the apparatus is termed a gas density balance, it is the specific gravity of the gas and not the density which is actually determined. The procedure given below is essentially the same as that outlined by the Bureau of Standards.

The gas and air were drawn slowly into the balance through tubes containing calcium chloride and phosphorous pentoxide to insure complete dessication. In making a determination the apparatus was first purged by drawing air in the balance, evacuating, and then repeating this process seven or eight times. A small pump, with which the pressure could be reduced to 20 to 25 cm. of mercury, was used for this purpose. At first the apparatus was washed by placing a slight vacuum on the balance and drawing the air (or gas as the case might be) through it. This method, however, required more gas and exhausted the drying chemicals too rapidly and was discarded in favor of the first named method. When the balance was sufficiently purged, it was filled with air and the pressure reduced until the pointer gave the desired reading. The reading was checked several times with air and the process repeated with the gas. The position at which the pointer is adjusted depends upon the gravity of the gas in question. For example, the Lawrence City gas has a gravity of .572 and, in determining the gravity of the gas, the beam was balanced so that the pointer was several points above the zero on the~~s~~ scale. In the case of a light gas, such as this, it is necessary to place the gas under pressure and the air under a vacuum in order to balance the beam at a suitable position. It is therefore advisable to select a practical point, such that neither the pressure nor vacuum used will be excessive, this precaution being taken to prevent leaks. The experiments were carried out in a room free from gas and temperature changes.

The pointer is adjusted to the desired position and the absolute pressure determined in each case. The gravity is then calculated from the following formula:-

$$\frac{Sg}{Sa} = \frac{P_1}{P_2}$$

Sg is the specific gravity of the gas, Sa the specific gravity of air, P_1 the pressure at which the beam balances in air, and P_2 the pressure at which the beam balances in the gas. The specific gravity of the air is taken as 1 and the formula then becomes -- $Sg = \frac{P_1}{P_2}$

Excepting the method of direct weighing this is the most accurate method of determining specific gravity. An accuracy of .1 to .3 percent is obtainable. A certain amount of skill in manipulation is necessary, but this can be developed by practice.

A typical run is shown in the following table:

Barometric pressure (millimeters).................		729.3
Gage readings with air (millimeters).............	(242.5 / 117.0	
Pressure (millimeters)...........................		-125.5
Total Pressure...................................		603.8
Gage Readings with Gas (millimeters).............	(338.5 / 12.7	
Pressure (millimeters)...........................		325.8
Total Pressure (millimeters).....................		1055.1
Specific Gravity.................................	$\frac{603.8}{1055.1}$ =	.5723

DIRECT WEIGHING METHOD

This method is the most standard way of determining gas density, but, unlike the previous methods, it requires more technique and precautions. The procedure for determinations by this method was as follows:- Two flasks with a volume of 206 cc. were used in the work, one being used as a counterpoise and one for weighing the gases. The gas was carefully dried before weighing by means of the drying tubes used with the gas density balance. The temperature of the gas was regulated by means of a constant temperature bath, the flasks being immersed in this bath for one half hour and then the pressure adjusted to that of the atmosphere by giving the stop cock on the flask one half turn so that the gas which had been previously placed in the flask under a slight pressure, would adjust itself to the pressure of the atmosphere. The flasks were then dried for one half hour in a dessicator and weighed, the balance being kept dry be means of a small jar of calcium chloride. The volume of the flask in which the gas was weighed was found by the following method:-

Weight of Flask and Water at 25°C...........	207.39 + C.P.	
Weight of Flask and Air at 25°C.............		1.96 + C.P
Approximate weight of air (200 cc. @ 25°)		.22
Weight of Flask.............................	1.74 + C.P.	
Weight of Water.............................	205.65	
Density of Water at 25°		.99704
Volume of Flask (No. of cc.s of water) $\frac{205.65}{.99704}$ =		206.3

When a suitable chemical balance and other chemical apparatus is at hand this method affords a reliable and accurate means of determining gas density. A typical run is shown in the table given below:-

Barometric Pressure	730 mm.	
Volume of Flask at 25°C	206.3 cc	
Weight of Flask+Gas at 25° and 730 mm.	1.8587 + C.P.	
Weight of Flask+Air at 25°, and 730 mm		1.9580 + C.P.
Weight of Air (206.3cc) at 25° and 730 mm		.2345
Weight of Flask	1.7235 + C.P.	
Weight of Gas at 25° and 730 mm	.1352	
Specific Gravity of Gas	$\frac{.1352}{.2345}$ =	.5723

CALCULATION FROM THE ANALYSIS

The accuracy of this method is dependent entirely upon the accuracy of the analysis. The accuracy of the analysis depends largely upon the technique of the analyst in manipulation of the apparatus and partly upon the type of apparatus used. For the analysis of the gases in the work the slow combustion method was used. The type of apparatus was identical with that used by Allen and Lyder in their work on the natural gases of Kansas and Oklahoma.[1] The calculation of specific gravity from the explosion method of analysis invariably gives lower results than the slow combustion method. This is due to the formation of oxides of nitrogen in the explosion analysis which gives the percentage of methane high and the percentage of ethane low. The explosion method is therefore not recommended for accurate work. For the most accurate analysis of hydrocarbons in gas the method of fractional distillation must be used. With gases such as the Lawrence City gas, however, which contains only a very small percentage of heavy hydrocarbons, and chiefly methane and ethane, a calculation of specific gravity from the combustion analysis introduces only a slight error. The specific gravity is calculated from the known specific gravity of the constituents that comprise the gas. In the analysis of natural gas the residue is calculated as nitrogen. With gases such as the Lawrence City gas, the residue is practically all nitrogen but with some high residue gases, such as are found near Dexter, Kansas, which contain 40 to 98 percent residue, a small percentage of helium[2] or other inert gas may be present with the nitrogen and in such

1. Engineering Bulletin #11, Uni. of Kansas.
2. Cady and McFarland, Geological Survey of Kansas, 9, 228 (1908)

case a slight error will be introduced unless the percent of such constituent is known. The method of calculating the gravity from the analysis is as follows:-

Constituents	Specific Gravity[1] of Constituents.		Analysis Lawrence Gas		
CO_2	1.5291	X	0.67%	=	.0102
O_2	1.1054	X	0.00	=	
CH_4	.5545	X	96.69	=	.5361
C_2H_6	1.0494	X	1.00	=	.0105
Residue (N_2)	.9674	X	1.64	=	.0159
Gravity of Gas (Air = 1).					.5727

1. Hamor and Padgett Examinations of Petroleum, Pg. 260.

The table[1] below gives the specific gravity of a number of gases and these values may be used for calculating the specific gravity of a gas (containing two or more of these gases) from an analysis which shows the percent of the different constituents.

GAS	FORMULA	SPECIFIC GRAVITY
Acetylene	CH⋮ CH	.906
Ammonia	NH_3	.597
Argon	A	1.38
Bromine	Br_2	5.87
Butane	$CH_3CH_2CH_2CH_3$	2.046
Carbon Dioxide	CO_2	1.5291
Carbon Monoxide	CO	.9670
Carbon Oxysulphide	COS	2.104
Chlorine	Cl_2	2.49
Cyanogen	N⋮C.C⋮ N	1.806
Dimethyl Ether	$CH_3.\ O.\ CH_3$	1.617
Ethane	$CH_3.\ CH_3$	1.0494
Ethylene	$CH_2:CH_2$	.978
Fluorine	F_2	1.31
Helium	He	.137
Hydrogen	H_2	.0695
Hydrogen Sulphide	H_2S	1.1895
Iodine	I_2	8.72
Krypton	Kr	2.818
Methane	CH_4	.5545
Neon	Ne	.674
Nitrogen	N_2	.9674
Nitrogen Monoxide (nitrous)	N_2O	1.5301
Nitrogen Dioxide (nitric)	$NO(N_2O_2.)$	1.0366
Oxygen	O_2	1.1054
Propane	$CH_3.CH_2.CH_3$	1.558
Propylene	$CH_3.CH:CH_2$	1.498
Silicon Fluoride	$Si\ F_4$	3.57
Sulphur Dioxide	SO_2	2.2639
Xenon	Xe	4.422

1. Van Nostrad's Chemical Annual - Fifth Issue 1922.

COMPARISON OF THE METHODS

The table below gives a comparison of the different methods which have been outlined for determining gravity.

METHOD	SPECIFIC GRAVITY OF LAWRENCE GAS	
	1	2
Effusion	.580	.579
Effusion (Corrected for water vapor)	.5716	.571
Edwards Gas Density Balance	.5723	.570
Direct Weighing	.5723	.570
Calculation from Analysis	.5726	.575

The gas density balance and direct weighing methods are taken as standards and it will be seen that results given by the two methods are comparable and show an accuracy of about 2 percent. The method of calculation from the analysis gave an accuracy of about .1 to .9 percent, the first of which more nearly represents the results that should be obtained. The effusion method gave an error of about 1.5 percent, due to the gas and air being saturated with water vapor. It will be noticed that by using the correction for water vapor, an accuracy of .1 to .2 percent is obtained. There are, however, other errors which are sometimes experienced when using the method and these are taken up somewhat in detail in the following part of the thesis.

Below is given a number of determinations similar to those given above and these results indicate about what might be expected on carefully made determinations. The results given by the effusion method are given on the gas saturated with water vapor while the other results are given on the dry gas. It will be noticed, however, that the results given by the effusion method are much the same as the true gravities obtained by direct weighing. This was mainly due to the characteristics peculiar to the particular apparatus used and such factors are discussed in the work that follows.

Direct Weighing	Edwards Gas Density Balance	Effusion	Calculation from analysis
.645	.646	.645	.631
	.652	.653	.656
	.638	.642	.635
.628	.625	.627	.612
	.606	.609	.604
.573	.570	.573	.575
.572	.571	.571	.573
.569	.569	.566	.579

THE EFFUSION METHOD

This method is widely used in commercial practice because of its simplicity, ease of operation, and the rapidity with which a determination can be made. As generally used, however, the time for effusion is taken on the gas and air saturated with water vapor which introduces a certain amount of error, varying with the temperature of the experiment and the true gravity of the gas. In the work that is to follow, the method was investigated as to the source of errors and the accuracy that can be obtained by varying the conditions of the experiment.

The method has been worked out much in detail by the Bureau of Standards.[1]

DERIVATION OF FORMULA USED

Before giving the experimental data and other work on the effusion method, a derivation of the formula used for calculating the specific gravity of a gas from the data obtained in an experiment will be given. As stated on page 6 the method was first used by Bunsen in his work on gases and is based upon the fact that the specific gravities of two gases escaping through an orifice or narrow opening in a thin plate have nearly the same ratio to each other as the square of their speeds of escape. This may be expressed by the formula $\frac{S_1}{S_2} = \frac{T_1^2}{T_2^2}$ where gas S_1 has a speed of escape T_1 and gas S_2 has a speed of escape T_2. Air is usually run as S_2 and regarded as 1 so that the equation becomes $S_1 = \frac{T_1^2}{T_2^2}$.

1. Tech. Papers of the Bureau of Standards, No. 94 and No. 359.

Details of operation of the apparatus and method of procedure for a determination are given on page 30.

The apparatus is shown diagrammatically in figure 1. The jar A is the effusion jar and is filled with air to a certain level b. Tube B is the effusion tube and e the platinum orifice. The time for effusion is taken for that volume of gas in the tube represented by the distance between the marks c and g on the effusion tube. This volume is represented by v which is the volume of gas effused. The water head at the start is represented by the difference between water level i and water level c of the effusion tube while the water head at the finish is represented by the difference between the water levels g and h.

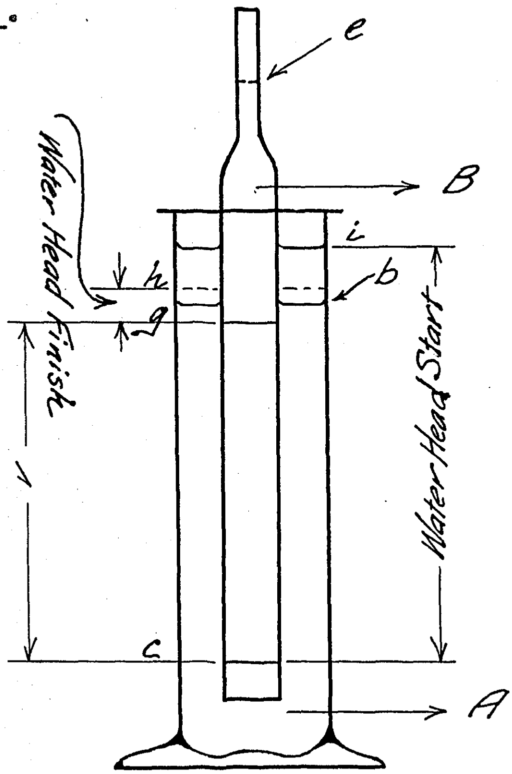


FIGURE 1

The work done by the water on the gas and air during effusion is the same in each case so that the formula for the specific gravity of the gas may be derived from the old established physics equation for work which states that "work" equals "mass" times the square of the "velocity." "M" represents the mass of the gas or air effused as the case may be and "V" represents the velocity of the effusing gas or air. Letting t equal time, d equal density, and S equal specific gravity (the subnumeral one in each case refers to gas and the subnumeral two refers to air) the derivation may be given as follows:

$$\text{Work} = M\,V^2$$

$$M_1V_1^2 = M_2\,V_2^2$$

$$\frac{M_1}{M_2} = \frac{V_2^2}{V_1^2}$$ and since the velocity is inversely proportional to the time

$$\frac{M_1}{M_2} = \frac{T_1^2}{T_2^2} \qquad d = \frac{\text{Mass}}{\text{volume}}$$ and letting the volume equal unity, the equation becomes

$$\frac{d_1}{d_2} = \frac{t_1^2}{t_2^2} \qquad S \text{ is proportional to } d$$

therefore $$\frac{S_1}{S_2} = \frac{t_1^2}{t_2^2} \qquad S = \text{air} = 1$$

and $$S_1 = \frac{t_1^2}{t_2^2}$$

Temperature and pressure must remain constant throughout the experiment or some error will be introduced due to this source. When water is used for the confining liquid, both the gas and air are saturated with water vapor so that, unless a correction is made, the apparent specific gravity may, under certain conditions, vary considerably from the true gravity. Such a correction is made as shown in a following paragraph on the effect of water vapor.

GASES USED IN THE WORK

The Lawrence City natural gas was principally used in the work but, to further investigate the accuracy and errors of the method, oxygen and hydrogen were also used.

DATE	SPEC. GRAVITY	DATE	SPEC. GRAVITY
2 - 16 - 22	.581	5 - 19 - 22	.578
2 - 17 - 22	.581	5 - 23 - 22	.580
2 - 18 - 22	.583	5 - 26 - 22	.584
2 - 21 - 22	.583	5 - 30 - 22	.577
2 - 24 - 22	.577	6 - 2 - 22	.579
2 - 27 - 22	.581	6 - 6 - 22	.585
3 - 1 - 22	.584	6 - 11 - 22	.582
3 - 3 - 22	.581	6 - 13 - 22	.583
3 - 7 - 22	.579	6 - 17 - 22	.575
3 - 10 - 22	.580	6 - 20 - 22	.585
3 - 14 - 22	.587	6 - 24 - 22	.581
3 - 17 - 22	.579	6 - 27 - 22	.580
3 - 22 - 22	.577	6 - 30 - 22	.584
3 - 25 - 22	.584	7 - 5 - 22	.578
3 - 28 - 22	.584	7 - 8 - 22	.577
4 - 1 - 22	.581	7 - 12 - 22	.574
4 - 4 - 22	.580	7 - 14 - 22	.580
4 - 7 - 22	.582	7 - 18 - 22	.581
4 - 11 - 22	.586	7 - 21 - 22	.580
4 - 17 - 22	.584	7 - 25 - 22	.578
4 - 21 - 22	.581	7 - 28 - 22	.582
4 - 25 - 22	.577	8 - 1 - 22	.578
4 - 28 - 22	.582	8 - 4 - 22	.577
5 - 3 - 22	.580	8 - 8 - 22	.586
5 - 10 - 22	.572	8 - 11 - 22	.581
5 - 13 - 22	.572	8 - 15 - 22	.574
5 - 15 - 22	.584	8 - 18 - 22	.579
5 - 16 - 22	.579	A V E R A G E	.580

NATURAL GAS

The natural gas used was the Lawrence City gas and the variation in gravity from time to time was slight. The results given on the preceding page show the variations in the gravity (uncorrected for water vapor) of the gas.

Determinations by means of the Edwards gas density balance showed that the true gravity of the gas varied from about .572 to .574 during the work. The methane content varied but little from 96 per cent and the ethane percentage was about one. A typical analysis of the gas is as follows:

Constituent	Per Cent
CO_2	0.67
O_2	0.00
CH_4	96.69
C_2H_6	1.00
Residue (N_2). . . .	1.64

OXYGEN

The oxygen was obtained from a tank of commercial oxygen made by the Linde process. An analysis of the gas showed the following content:

Constituent	Per Cent
Oxygen	99.0
Residue (N_2)	1.0
Specific Gr. (Calc. from analysis)	1.103

HYDROGEN

The hydrogen used was made by electrolysis, a low current being used so as to get a good product. An analysis of the gas was as follows;

Constituent	Per Cent
Hydrogen	98.48
Oxygen	.35
Residue	1.17
Specific Gr. (Calc. from analysis)	.0836

The hydrogen, after being made, became contaminated and showed a gravity of .171.

ORIFICES USED IN THE WORK

Orifices of various sizes and shapes were made for use in the work and in the work that follows tests are given that show the variation in results when using the different orifices. A number of different sizes were made so as to have a suitable size for the different sized bulbs. A set of orifices of varying degrees of roughness were also made to determine the effect of burrs.

The method used by Hempel[1] for making orifices for such work was to pierce a hole in the platinum foil with a fine sewing needle and then hammer it with a polished hammer on a polished anvil. This method could at best leave but an irregular opening. The method used in this work for making the orifices was to pierce the platinum foil with a very fine needle and then grind it with a fine carborundum stone until the orifice was free from burrs. The progress was noted under the

1. Hempel - Gas Analysis - Trans. by L. M. Dennis. Pg. 269.

microscope and by continued grinding a smooth and regular orifice could be obtained which was quite satisfactory. The photomicrographs of orifices No. 7 and 16 shown on page 44 are typical of the orifices used in the work. The platinum foil containing the orifices, ground to shape, was cut out in the shape of a circular disk with the orifice in the center and the disk sealed into a glass tube so that the finished orifice tip appeared as shown in figure 2 (a). Characteristic orifice shapes are shown in figure 2 (b). By grinding on both sides, as was done, at least a very close approximation to (c) was obtained, (c) being the ideal type of orifice. The ideal orifice, (c), is in reality a vertical cylindrical hole through the platinum foil and should be the shape of orifice used for effusion work. Type (a) and (b) are characteristic shapes obtained when the platinum plate is not properly ground. Orifice No. IX is one of this type, IX-A being similar to (a) and IX-B similar to (b).

Three different thicknesses of platinum foil were used in the course of the work, the thickness being .0005 in., .0008 in. and .001 in. The foil .0005 in. thick was too thin and would often wrinkle and grind through in other places before the orifice was ground free from burrs. The foil .001 in. thick seemed to be slightly too heavy and was

FIGURE 2 (a)

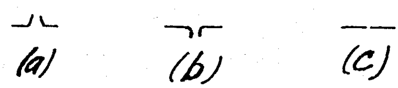


FIGURE 2 (b)

difficult to grind free from burrs while that .0008 in. thick gave very satisfactory results and was used for making most of the orifices. The diameter of the orifices was measured by means of a micrometer microscope. A list of the orifices used in the work, stating the size and whether or not they were regular, is given below. A and B refer to the two ends of the orifice tips and are the same in the case of the regular orifices but show some variation with the irregular ones.

ORIFICE NUMBER	DIAMETER	REMARKS
I	.31 millimeter	Regular
IV	.21 "	"
V	.12 "	"
VI	.08 "	"
VII	.17 "	"
VIII	.24 "	Burrs
IX	.24 "	Not Ground
X	.24 "	Burrs
XI	.27 "	"
XII	.30 "	"
XIII	.24 "	Irregular
XIV	? "	Rough and irregular
XV	? "	Burrs
XVI	.16 "	Regular
XVII	.15 "	"
XVIII	.21 "	"

These Orifice Numbers will be referred to in the work that follows.

VARIATIONS AND ACCURACY OF THE EFFUSION METHOD, USING WATER AS THE CONFINING LIQUID

The various factors which introduce error in the effusion method are discussed somewhat in detail. Though at times these errors are considerable the method seems to be the most satisfactory for field work, because of its simplicity, ease of manipulation and the rapidity with which a determination can be made. With proper precaution and manipulation satisfactory results can be obtained.

TYPE OF APPARATUS

Though several slightly different types of apparatus were used in the work, the type described below was used for the most of the work and proved to give satisfactory results.

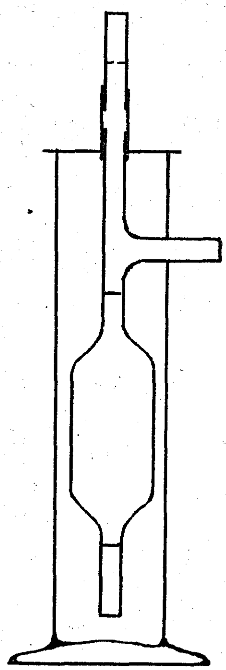


FIGURE 3

Figure 3 shows the type of apparatus used. It can be made by cutting off the delivery end of a 50 cc. pipette so as to give the desired length and then sealing a short tube on the side, forming a T. A glass cylinder, slightly larger than the pipette, was used for the outer cylinder. A hole was bored in the cylinder through which the side tube extended, as shown in the figure. The side tube was fastened into the cylinder rigidly, by a stopper or other means and this served to hold the pipette in place. In case no hole is bored in the cylinder, the side tube can be raised above the top of the cylinder and the pipette held in place in the cylinder by means of a large cork stopper. The platinum orifice tip, which consisted of a glass tube with a platinum orifice sealed in it as shown in figure 2 (a) page 28, was fastened to the pipette by means of a rubber tube and the top was closed by means of a rubber ~~type~~ tube and pinch cock. A rubber tube and pinch cock or glass stopcock was used for closing the inlet. The pipette was marked above and below the bulb, as shown in the figure, and the time of effusion was taken for the amount of gas represented by the volume between these two marks. Care was taken to keep the pipette clean so that no error would be experienced in the tests due to water adhering to the glass. The apparatus was connected to a gas apparatus or leveling bulb device so that it might be filled with air or gas for the testz. The method or operating was as follows: - The apparatus is purged by opening the inlet and filling the bulb with air, letting this air escape and then repeating the process a few times. The orifice tip is then closed with the pinchcock, the pipette filled with air and the inlet closed. The pinchcock is taken off the orifice tip and the time of effusion taken for the air. The result is checked several times and the process repeated for the gas in question. This type of apparatus was very satisfactory and gave consistent results. Results of tests, page 25, on the Lawrence gas, which varied but little from time to time, show the consistency of the apparatus. The apparatus can be made by simple glass blowing and assembling of the different parts which are obtainable at most any chemical laboratory.

EFFECT OF WATER VAPOR: - When water is used in the apparatus as the confining liquid, it is apparent that both the gas and air will be saturated with water vapor. The results obtained will therefore give the gravity of the gas uncorrected for water vapor. The error due to this source will necessarily vary with the true gravity of the gas and the temperature of the experiment.

APPARENT SP. GR.	SPECIFIC GRAVITY - CORRECTED FOR WATER VAPOR					
	15° C.	% Error	20° C.	% Error	25° C.	% Error
.1000	.0901	9.00	.0865	13.50	.0820	18.00
.2000	.1912	4.40	.1880	6.00	.1840	8.00
.3000	.2923	2.57	.2895	3.50	.2860	4.67
.4000	.3934	1.65	.3910	2.25	.3880	3.00
.5000	.4945	1.10	.4925	1.50	.4900	2.00
.6000	.5956	.73	.5940	1.00	.5920	1.33
.7000	.6967	.47	.6955	.64	.6940	.86
.8000	.7978	.28	.7970	.38	.7960	.50
.9000	.8989	.12	.8985	.17	.8980	.22
1.0000	1.0000	.00	1.0000	.00	1.0000	.00
1.1000	1.1011	-.10	1.1015	-.14	1.1020	-.18
1.2000	1.2022	-.18	1.2030	-.25	1.2040	-.33
1.3000	1.3033	-.25	1.3045	-.35	1.3060	-.46
1.4000	1.4044	-.31	1.4060	-.43	1.4080	-.57
1.5000	1.5055	-.39	1.5075	-.50	1.5100	-.67

In using the effusion apparatus with water for the confining liquid the gravity should therefore always be corrected for water vapor. The correction table for water vapor given on the preceeding page was calculated from the equation given on page 35 and will show the variation of the apparent gravity from the true gravity. Apparent gravities within the range given but not shown in the table may be obtained by interpolation. This data is given on page 34 in the form of a curve.

A derivation of the formula used to correct the specific gravity for water vapor is given in Technologic Paper No. 94 of the Bureau of Standards. The formula as derived is given below:

Letting S = Specific Gravity

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

dw = Density of water vapor

($\frac{dw}{da}$ assumed to be .622)

dg = Density of gas (equals Sda)

da = Density of air

p = Pressure of gas and air

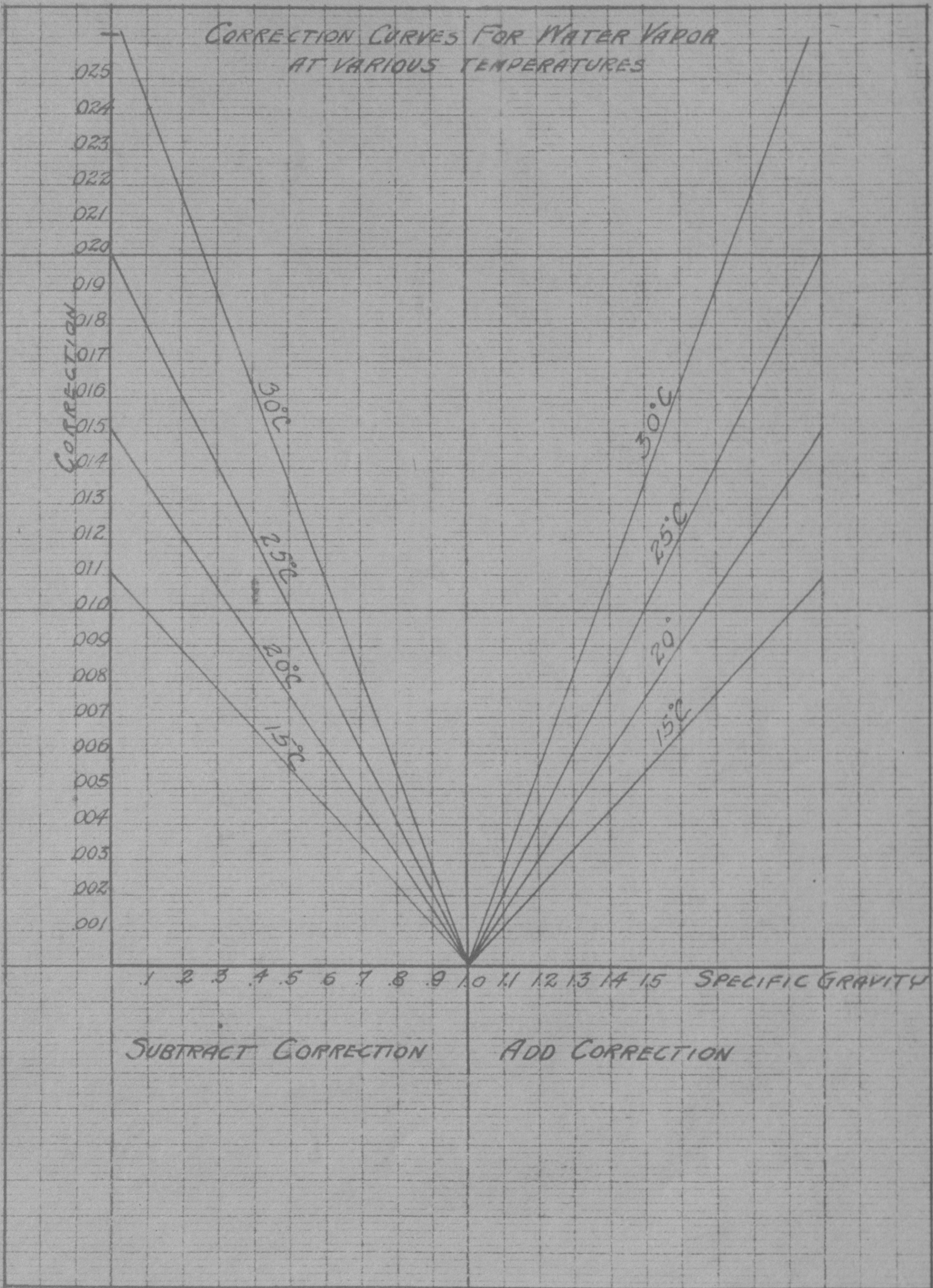
pw = Partial pressure of water in question

k = Constant

Then $k = \frac{dwpw}{da\ (p-pw)}$

and $S_s = \frac{S+k}{1+k}$

The variations due to variation in pressure are so small at ordinary pressures that no correction is made for errors due to this



CORRECTION CURVES FOR WATER VAPOR
AT VARIOUS TEMPERATURES
CORRECTION
.025
.024
.023
.022
.021
.020
.019
.018
.017
.016
.015
.014
.013
.012
.011
.010
.009
.008
.007
.006
.005
.004
.003
.002
.001
30°C
25°C
20°C
15°C
30°C
25°C
20°
15°C
.1 .2 .3 .4 .5 .6 .7 .8 .9 1.0 1.1 1.2 1.3 1.4 1.5
SPECIFIC GRAVITY
SUBTRACT CORRECTION
ADD CORRECTION

source. The values of k for different temperatures are given in the table below so that in making a determination it is only necessary to record the temperature of the water in the apparatus with the effusion data and then substitute the value for k given in the table and the apparent specific gravity (calculated from the effusion data) in the formula above to obtain the true gravity. To illustrate the use of the table:- If the apparent gravity of a gas as found from the effusion data is .700 at 25°C then the true gravity will be:

$$.700 = \frac{S \text{ plus } .02}{1 \text{ plus } .02} \quad \text{or } S = .694$$

VALUES FOR k AT 760 mm AND VARIOUS TEMPERATURES:

$$k = \frac{dwpw}{da\,(p-pw)}$$

Temperature °C	k
0	.004
5	.005
10	.008
15	.011
20	.015
25	.020
30	.027
40	.048
50	.086
60	.151

To show the error introduced due to water vapor, experimental results were obtained on the gravity of the Lawrence City gas, oxygen, and hydrogen at different temperatures in which tests the amount of water vapor in the gas varied. The results of the tests are given in the table - I, page 37.

The percentage error is calculated on the true gravity of the gases, which is 1.103 for Oxygen, .572 for the Lawrence gas and .171 for the hydrogen. It will be noticed that the results for oxygen are but slightly in error and vary only to a small extent at the different temperatures. The results given on the natural gas and hydrogen, however, are considerably in error at the higher temperatures. It is evident that at the higher temperatures the amount of water vapor in the saturated gas will be greater. The presence of this water vapor as shown by the table on page 37 will cause the apparent gravity to be larger than the true gravity for gases below 1 and smaller for gases with a gravity above 1. The per cent error is also shown to increase with an increase of temperature in the case of the natural gas and hydrogen which are much below one while with the oxygen which has a gravity only slightly above one the error is small at all the temperatures. From the date, it can readily be seen that the apparent gravity should always be corrected for the water vapor present and the resulting value reported as the specific gravity of the dry gas. The specific gravities given in table I on the following page are given in table II page 37 with the true gravities calculated to the gravities of the gases saturated with water vapor at the various temperatures.

TABLE - I

TEMPERATURE °C	OXYGEN Air Time Sec.	O_2 Time Sec.	Specific Grav.	% Error	LAWRENCE GAS Air Time Sec.	Gas Time Sec.	Specific Grav.	% Error	HYDROGEN Air Time Sec.	Gas Time Sec.	Specific Grav.	% Error
30	101.6	106.6	1.101	-.2	103.4	78.8	.5819	+1.7	112.9	50.3	.1986	+.16.1
40	99.9	104.6	1.097	-.6	101.7	77.8	.5852	+2.3	103.6	49.0	.2237	+30.8
50	98.0	102.9	1.103	.0	98.8	77.4	.6137	+7.3	101.2	49.4	.2382	+39.3
60	95.5	100.00	1.097	-.6	97.5	76.7	.6189	+8.2	97.2	53.4	.3029	+77.0

TABLE - II

Temp. °C	OXYGEN Apparent Sp. Gr.	S_s Calculated	% Error	LAWRENCE GAS Apparent Sp. Gr.	S_s Calculated	% Error	HYDROGEN Apparent Sp. Gr.	S_s Calculated	% Error
30	1.101	1.100	+.1	.5819	.5832	-.2	.1986	.1928	+2.9
40	1.097	1.098	-.1	.5852	.5916	-1.1	.2237	.2090	+7.0
50	1.103	1.095	+.7	.6137	.6059	+1.3	.2382	.2366	+.8
60	1.097	1.090	+.6	.6189	.6281	-1.4	.3029	.2798	+8.2

The apparent gravities in most of the above cases check at least fairly well with the calculated (S_s) values, an error of about 1.0 to 1.5% being considered a fair check. It must always be remembered however, that when using water for the confining liquid there is likely to be some condensation of water vapor at the orifice opening and considerable error may at times be introduced from this source. Such may be taken as an explanation of the errors in the apparent gravities given for hydrogen. To avoid the error due to water vapor, sulphuric acid and mercury[1] have been used by some workers. Both of these methods , however, have their disadvantages in that they are not always practical. For field work the sulphuric acid requires too much care and is dangerous to handle on account of acid burns. It also is not always available for use. In the use of mercury, a much greater effusion pressure is obtained which considerably reduces the time of effusion. The stop watch method of timing, therefore, becomes quite inaccurate and a more exact method, such as automatic timing with a chronograph, or other apparatus, is required for accurate work. Such a device would, therefore, make the method impractical for field work. This method is taken up more in detail in a later paragraph of the thesis.

THE EFFECT OF A VARIATION IN WATER HEAD: The variation in water head was determined using orifice XVI-A on the 45 cc. bulb (apparatus made with the 50 cc pipette) and varying the head of water. The determinations were made on the Lawrence City Gas, using the apparatus with the 45 cc. bulb and orifice XVI-A. Results were as follows:

1. Hempel Gas Analysis, Trans. by L. M. Dennis Pg. 269, Tech. Paper of the Bureau of Standards No. 94

RUN	WATER HEAD		SPECIFIC GRAVITY	% ERROR
	START	FINISH		
1	143 mm.	7 mm.	.576	- .7
2	153 mm.	17 mm.	.578	- .3
3	163 mm.	27 mm.	.576	- .7
4	174 mm.	36 mm.	.581	.2
5	184 mm.	44 mm.	.573	-1.2
6	194 mm.	54 mm.	.578	- .3

The per cent of error is calculated on the apparent specific gravity, of .580, which is the average of the determinations made on the Lawrence gas. The 5th run gave a low result but the others checked within reasonable limits. There is evidently no noticeable variation due to water head when using the variation given. When using the lower water head, however, care must be taken to prevent drafts and downward currents of air since these would have a measurable effect. For field work, therefore, a larger head is much more important than in laboratory work, because there is much more chance of errors due to drafts. It is advisable, therefore, to use a water head of at least 1 to 2 inches. A later paragraph in the paper is devoted to the effect of drafts on the effusion time. Edwards, in his work with the Bureau of Standards[1] says that a low effusion pressure is to be avoided but that a higher pressure does not always give any better results.

1. Technologic Paper of the Bureau of Standards No. 94.

VARIATIONS DUE TO THE SIZE OF BULB: - Four different sizes of bulbs were used to determine if the results showed any variation. Different sizes of orifices were also used to obtain a satisfactory and uniform effusion time. The results obtained were as follows: -

ORIFICE No.	DIAMETER MM.	VOLUME OF BULB CC.	WATER HEAD START MM.	WATER HEAD END MM	EFFUSION TIME FOR AIR Seconds	GRAVITY OF GAS	% ERROR
VI A	.08	8.6	144	4	86	.576	- .7
V A	.12	25	140	3	78	.570	-1.7
XVII A	.15	45.5	160	4	101	.584	+.7
IV A	.21	118	133	5	140	.578	- .3
VI A	.08	8.6	149	9	86	.566	- 2.4
V A	.12	25	132	9	78	.574	- 1.5
XVII A	.15	45.5	165	9	101	.571	- 1.5
IV A	.21	118	129	9	140	.580	0.0

The error with some of the stop watch readings was .5 per cent while with the most of the readings it was. 3 per cent and less. The percentage error in the gravity is calculated on the apparent gravity of the gas (gas saturated with water vapor or .580). Orifice IV - A with the 118 cc. bulb gave the best results. The 45 cc. bulb also gave good results in the first run while the two smaller bulbs with the smaller orifices gave low results. It is advisable, therefore, not to use a bulb smaller than 50 cc. The use of a small bulb requires the use of a smaller orifice which, within certain limits is not advisable, in that dirt particles are more likely to cling to the orifice and the condensation of water vapor is likely to be greater. In the work in general the 50 cc. bulb gave the best results and it may be said that either this size or a 100 cc. should be used with a suitable orifice, so that the effusion time will be 90 to 120 seconds.

VARIATION DUE TO THE SIZE OF ORIFICE: - The 45 cc. effusion tube was the most suitable size tube to use for the work. The gravity of the Lawrence City gas and of the commercial oxygen was determined using this size of effusion bulb, with different sizes of orifices. The error in stop watch readings is given in the table and is the highest variation of any one of the readings from the average reading.

ORIFICE		PER CENT ERROR IN READINGS				GRAVITY			
NUMBER	SIZE mm.	AIR	GAS	AIR	O_2	GAS	% ERROR	O_2	% ERROR
VI A	.08	.3	.3	.2	.1	.570	- 1.7	1.066	-3.4
V A	.12	.2	.3	.3	.2	.569	- 1.9	1.112	+.6
XVII A	.15	.8	1.0	.7	.3	.592	+2.1	1.069	-3.2
XVI A	.16	1.0	.3	.2	.2	.588	+1.4	1.040	-5.9
IV A	.21	.2	.0	.4	.2	.581	+ .2	1.101	- .4

The percentage error is calculated on the apparent gravities, or .580 for the gas and 1.105 for the oxygen. It will be noticed in the above table that most of the stop-watch readings checked within reasonable limits. With orifice XVII the readings on air and gas, and with orifice XVI the readings on air, checked for the first two or three runs and then the time increased and the runs checked again. The readings for gas on one of the runs with XVII seemed to rise slowly. They were as follows: - 76.0, 76.0, 76.6, 76.8, 76.8, 77.0 and 77.0 seconds. This rise can no doubt be explained by the condensation of water vapor. The variation in the readings for air cannot be explained in the same manner but may be due to drafts in the vicinity of the experiment or due to the lodging and dislodging of dust particles. The readings were as follows: - 101.0, 101.2, 100.8, 100.0, 100.4, 100.8, 100.8, and 100.2. The gravity of the natural gas as determined by use of the smaller orifices..08 and.12.was more nearly like the true gravity of the gas but it should check with the gravity of the gas saturated with water vapor which is given above. Orifice IV A gave good results in the determinations. It was also used to quite a large extent for taking gravities and always proved satisfactory. In work done by the Bureau of Standards[1], an orifice of .25 mm. in diameter is stated to give the best results. The design of apparatus, however, was somewhat different from that used in this work. Inaall the experiments orifice IV A, which had a diameter of .21 mm. gave the most satisfactory results.

<u>THE EFFECT OF BURRS</u>: - To determine what effect burrs and irregularities in the shape of the orifice had on the apparent gravity, eight orifices were made with varying degrees of roughness. They were all made with about the same size opening so as to obtain as near as possible the same accuracy in stop watch readings and to eliminate any error due to a variation in size. The 118 cc. bulb was used with a water head of 121 mm. at the start and 6 mm. at the end. The gravity of the Lawrence City gas and of the

1. Technologic Paper 94.

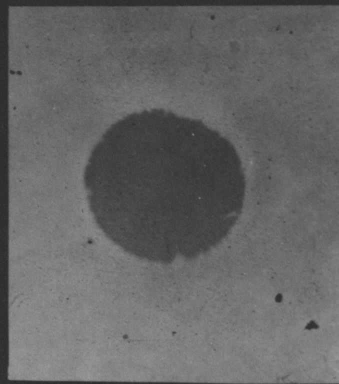
oxygen was taken using six different irregular orifices, and one regular orifice. The results obtained in the experiments were as follows: -

ORIFICE	SIZE mm.	REMARKS	LAWRENCE GAS		OXYGEN	
			GRAVITY	% ERROR	GRAVITY	% ERROR
XIV A	.?	Irregular	.582	.3	1.108	.3
X A	.24	Burrs	.588	1.4	1.108	.3
XII A	.30	Burrs	.599	3.3	1.097	.7
XIII A	.24	Irregular	.594	2.4	1.104	- .1
XV A	.?	Burrs	.585	.9	1.102	- .3
VIII A	.24	Burrs	.585	.9	1.100	- .5
IV A	.21	Smoothe	.578	- .3	1.104	- .1

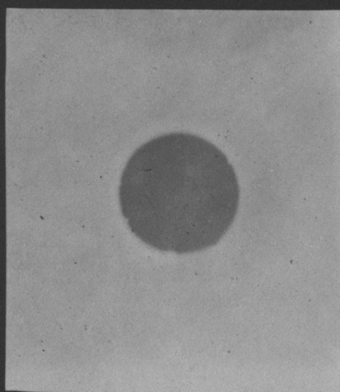
The specific gravity of the gases is calculated on the gravity of the gases saturated with water vapor, which is .580 for the Lawrence gas and 1.105 for oxygen. Photomicrographs were taken of the irregular orifices and also of a few of the typical orifices which were ground smooth and were free from burrs and irregularities. They are shown on the following pages.

There seemed to be no definite relation between the degree of irregularity or roughness of the orifices and the specific gravity. In fact, it was surprising that orifice XIV, which was the most irregular of all the orifices should give an accuracy of .3 per cent, which is as high a degree of accuracy as might be expected from any water type of the effusion apparatus. The orifice had, as shown in the photograph on page 45, besides the large irregular orifice several smaller openings.

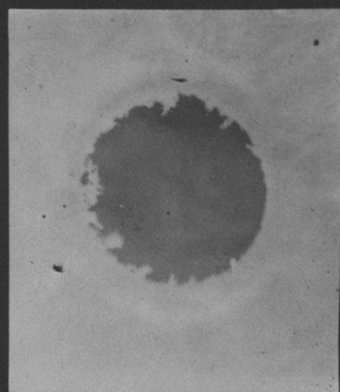
Orifice No. XIII



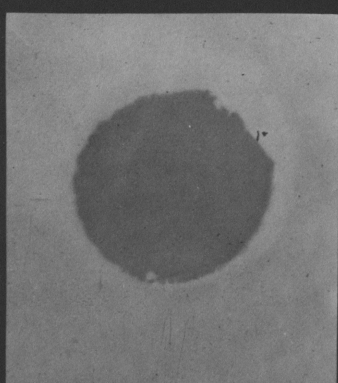
Orifice No. VIII



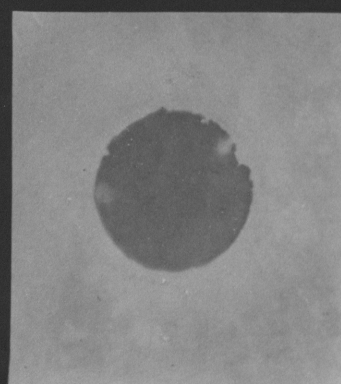
Orifice No. VII



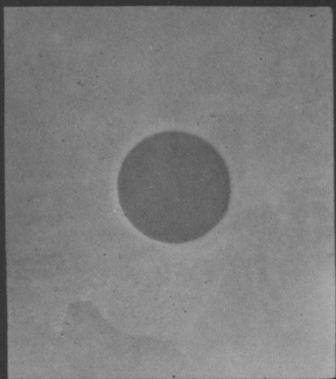
Orifice No. XI



Orifice No. XII

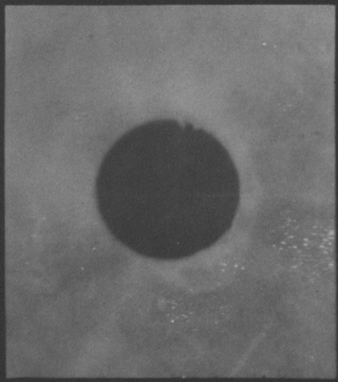


Orifice No. X

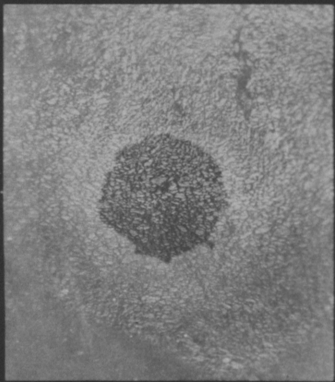


Orifice No. XVI

Orifice No. XIV



Orifice No. XVIII



Orifice No. XV

Orifice XIII, which gave a high result with natural gas, had a crack in the platinum fòil which extended for some distance away from the orifice. Orifice XII A, which had only burrs around the edge of the orifice, gave the highest percentage of error of any of the orifices. All the results given with oxygen were quite satisfactory. It would seem from this that no special precaution necessarily need be taken to make the orifice regular. This cannot be entirely true, however, for if burrs are left on the orifice they will catch fine dust particles which are likely to be in the escaping air or gas and in such case will give an inaccurate effusion time. Any condensing water vapor also will be more likely to cling to the burrs and cause an inaccuracy in the effusion time.

THE EFFECT OF DRAFTS IN THE EFFUSION METHOD: - To note the effect of drafts on the results obtained by the effusion apparatus, an electric fan was used to give the desired draft. The fan was set in different positions to get the effects shown in the accompanying figure. results were obtained for the three positions of the fan, 1, 2 and 3. In position 1, results were obtained for the three speeds of the fan to obtain any variation due to the amount of draft. The results obtained in the experiments are given in the following table.

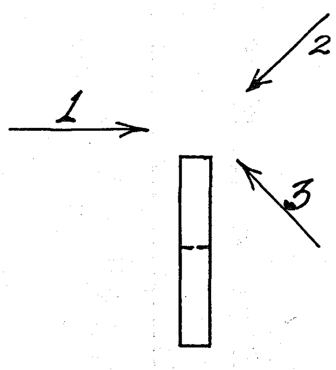


FIGURE 4

POSITION Of DRAFT	SPEED Of FAN	AIR TIME (Seconds)	GAS TIME (Seconds)	LAWRENCE GAS	
				GRAVITY	% ERROR
No Draft	----	79.1	60.1	.577	----
1	1	79.1	60.1	.577	----
1	2	79.4	60.2	.575	- .3
1	3	79.4	60.2	.575	- .3
2	2	79.9	60.9	.581	+.7
3	2	80.4	61.0	.576	- .2

The errors were calculated on the value of .577 or the result obtained by apparatus when there was no draft near it. The allowable error is about .3 per cent, so that all results except those for the test in which position 2 was used may be said to be satisfactory. The effect of the draft would no doubt be to increase or decrease the time for air and gas by a certain amount due to slight variations of pressure caused by the draft, and this amount would likely be the same in both cases. For example, the results obtained when the fan was in position 2, show a time for both air and gas which is .8 seconds higher than the times given for the air and gas in the tests with which no draft was used and this gave an error of .7 per cent.

These results will show the effect that drafts may have on the specific gravity. It seems, therefore, that a draft will not necessarily introduce an error, since with all but one of the tests the error was slight. There may be, however, other factors to consider, such as temperature changes and the liability of dust being caught in the draft and some of it lodging in the orifice. Another factor to consider is the type of orifice tip used. Figure 5 shows two types of orifices which are commonly used. The type of orifice (a), which was used in the tests, is the type generally used and is the more satisfactory type (b) being much more liable to give inaccurate results, especially when the orifice tip is in the vicinity of drafts. It is apparent that with type (a) the drafts cannot come in direct contact with the escaping gas, while with type (b) such can be the case. Type (a) should, therefore, be used with the effusion apparatus.

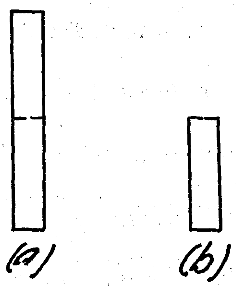


FIGURE 5

METHOD OF USING MERCURY AS THE CONFINING LIQUID IN THE EFFUSION METHOD

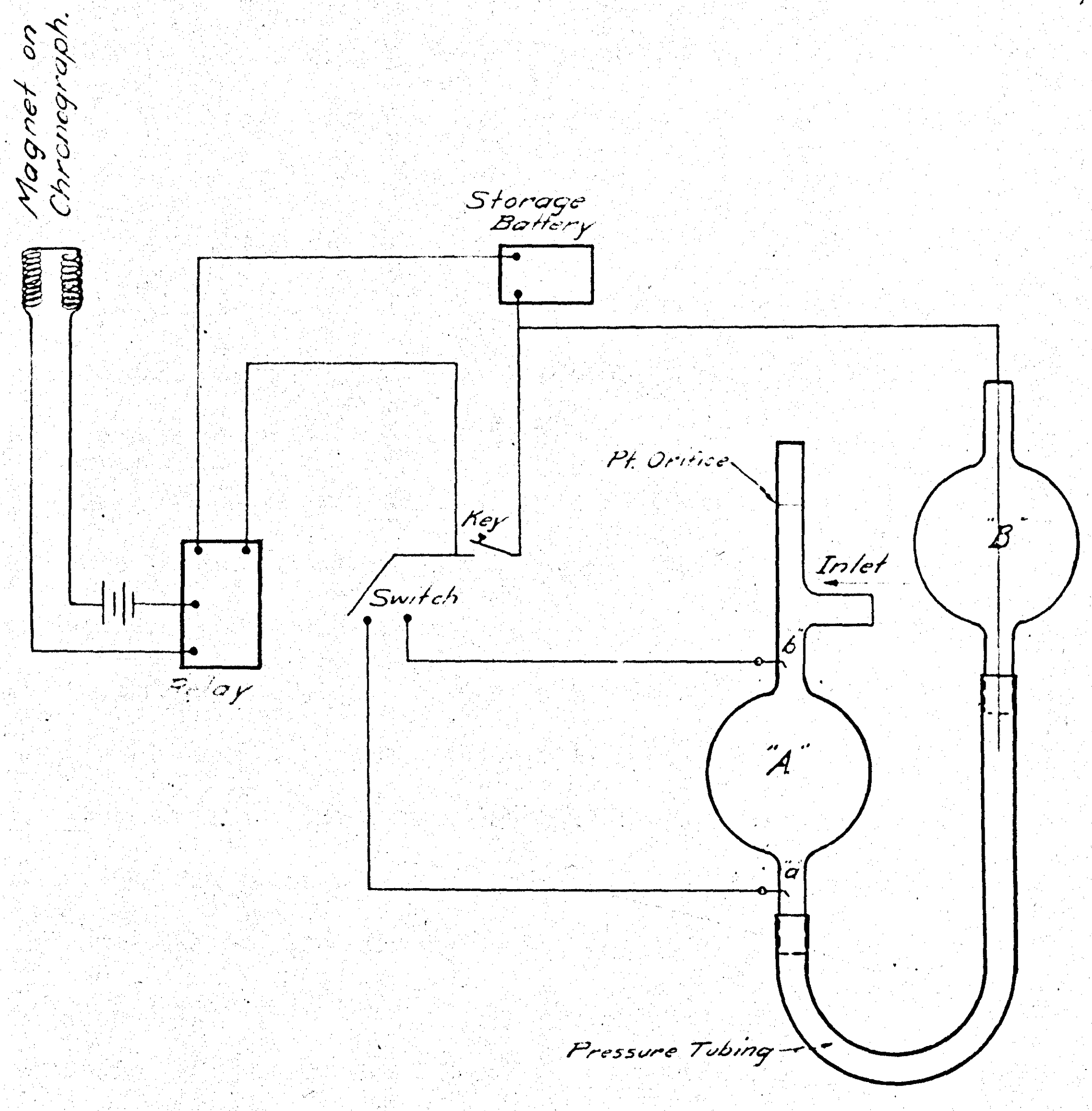
When mercury is used as the confining liquid, the error due to water vapor is eliminated. It is evident that the gas and air will be saturated with mercury vapor but the vapor pressure of mercury is so low at ordinary temperatures that the error is inappreciable. The formula $Sg = \frac{(t_1)^2}{(t_2)^2}$ is in reality only an approximate ratio but by using mercury as the confining liquid and avoiding possible errors due to sources other than water vapor, a satisfactory degree of accuracy can be obtained.

The effusion pressure, when using mercury, is considerably increased and the effusion time, likewise, decreased according to the size of orifice used. It is, therefore, necessary for accurate work to use some automatic timing device. In this work a chronograph apparatus was used for observing the time of effusion. The chronograph had a rotating drum on which the record sheet was placed and could be calibrated to read in seconds. It is not necessary, however, to have the sheet calibrated, since the values are only relative and may be measured with an engineer's scale and given in inches. The lines which represent the effusion time were measured to .01 to .02 inches, which represents a time of about .02 to .04 second. Ordinarily, results could be checked within reasonable limits.

The chronograph[1] used was made by Val Arntzen of Berkley, California and is considered to be a very good instrument, being the type that is ordinarily used in any observatory recording the time of observations. It is much larger than the tape chronographs but the record sheet used is much more convenient to file. The apparatus consists of a drum rotated by a weight clock work, which drum can be rotated at the rate of one or two revolutions per minute. An electro magnet carrying a pen makes a trace on the sheet which is wrapped around the drum. The chronometer causes a break in the circuit every second thus producing a break in the trace. This, therefore, enables the observer to scale the time as recorded on the sheet. More details concerning the apparatus may be found in the reference.

The apparatus used and system of wiring are shown on page 50. The two contact points were made of platinum wire and were sealed above and below the effusion bulb, as shown, The bulb B is the leveling bulb and sets upon a stationary support. A glass T tube was sealed above the

1. Campbell's Practical Astronomy.



WIRING DIAGRAM OF MERCURY EFFUSION Apparatus.

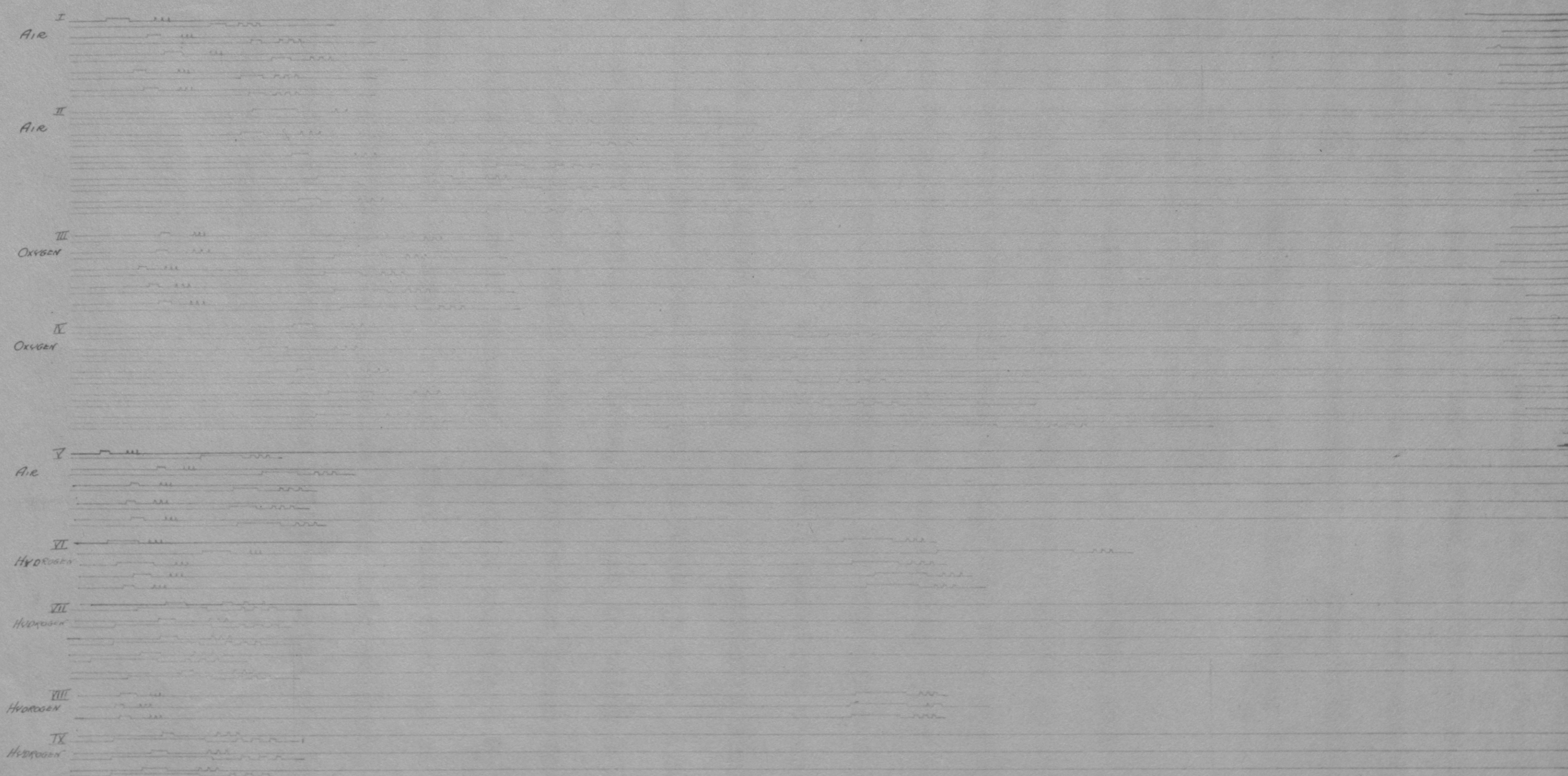
FIGURE 6

the effusion bulb A and the platinum orifice tip sealed to the tube above the T. A rubber tube is fastened to the inlet T and the inlet closed by means of a pinchcock. The orifice tip is also closed at the top by means of a rubber tube and pinchcock. The two bulbs are connected by means of rubber pressure tubing so that bulb B can be moved from its support for use as a leveling bulb in filling the apparatus with the desired gas.

The system of wiring is also shown in the diagram on page _____. The apparatus is wired so that when the mercury touches the platinum contact point below the bulb the circuit is completed. The switch is then opened and the circuit broken, the circuit being again completed when the mercury touches the platinum contact point above the bulb.

The proceedure for making a determination was as follows: Air which was previously dried by means of calcium chloride and phosphorous pentoxide, was drawn into the apparatus by lowering the leveling bulb, allowed to escape through the orifice and this process repeated several times until the apparatus was sufficiently purged. The apparatus was then filled with air, the orifice tip closed with the pinch cock, and the leveling bulb placed on its support. The cylinder on the chronograph apparatus was set revolving and the marker set in place. The pinch cock was then removed from the orifice tip and the air allowed to escape. The switch was set so as to make contact with point a, figure 6, at the start and when the mercury reached this contact point, the marking pen would jump to the side, the switch was then thrown open and the pen would jump back. The switch was then set to make contact with point b, figure 6, and the same process repeated with the second contact point on the bulb as with the first. The key which was in the circuit was used for marking the

CHRONOGRAPH SHEET No. 4



GSM 22

beginning and end of a run, three short dashes after a dash showing contact denote the beginning of a run and three long dashes denote the end. A typical chronograph sheet giving the results of a number of runs is shown in the figure on page 52. This same procedure was then followed with the gas and the results were calculated by the following formula:

$$Sg = \frac{(\text{ Length of line for gas in inches })^2}{(\text{ Length of line for air in inches })^2}$$

Results obtained by this method of determining specific gravity are given in the table on the following page. The results given in this table show that the results obtained are more nearly like the true gravity than results obtained when using water as the confining liquid. This is, of course, due to the fact that with the mercury the gas and air are both in a dry state. It is advisable to use this method therefore whenever it is practical and since it is quite essential that an automatic timing device be used, the method is practical only for laboratory use. The effusion time for the runs was thirty seconds and less, so that in using a stop watch, the error in the readings would ordinarilly be too large for the accuracy desired. While the use of mercury affords a satisfactory and more accurate method, it must be kept in mind that such factors as mercury head, size of bulb, temperature, etc., must be taken into account. The conditions given and methods of operating are believed to be the best for obtaining the desired results.

Orifice		Mercury Head mm.		Length of Line On Chronograph Sheet Inches			Lawrence Gas		Oxygen	
No.	Diameter mm.	Start	End	Air	Gas	Oxygen	Sp. Gr.	% Error	Sp. Gr.	% Error
XVII	.17	.135	9	23.56	17.90		.577	.7		
XVII	.17	135	9	46.94	35.59		.574	.0		
XVII	.17	135	9	23.55		24.71			1.101	-.2
XVII	.17	135	9	46.84		49.13			1.100	-.3
IV	.21	135	9	15.84		16.66			1.106	.3
IV	.21	135	9	31.68		33.22			1.100	-.3

GENERAL CONCLUSIONS

1. The Gas Density Balance method and Direct Weighing Method for determining specific gravity of gases are recommended when accuracy is the important factor in the determination. The first method is adapted to either field or laboratory use, the apparatus being made in two types, field and laboratory, while the second method can only be used in laboratory work. Both the methods afford an accuracy of .1 to .3 percent but require a certain amount of technique and are not advisable for use except by an experiended analyst. Techinque of operation of the Gas Density Balance (Edwards) can, however, be developed without a great amount of practice and this method is recommended as a standard for field work while either of the above mentioned methods can be used as a standard for laboratory work.

2. The accuracy of the method of calculating the specific gravity from the analysis depends entirely on the accuracy and completeness of the analysis. The method is recommended only when the analysis is made by an experienced analyst; when a complete analysis of the gas is at hand; with natural gas when the combustion method is used providing the residue is practically all nitrogen and the total hydrocarbons low in higher hydrocarbons (in other words the natural gas should be low in residue and high in methane); with natural gas also when the method of fractional distillation is used for the analysis. It is well to remember, however, that gravity calculations of the hydrocarbon constituents compensate to a certain extent. This is explained by the fact that the percentage of the hydrocarbons is often in error (the percent methane being high and that of ethane being low) due to the absorption of carbon dioxide formed in the combustion and the variations of the percentages of hydrocarbon

constituents are usually such that they compensate to a certain extent. An accuracy of .1 to .3 percent is often obtained under such conditions as are mentioned above, though ordinarily the degree of accuracy is not so high. The method is not recommended for use with an explosion analysis because of the formation of nitrogen oxides which introduces considerable error.

3. The above three methods can be used as standard methods for determining specific gravity Ithe method of calculation from the analysis only under the conditions mentioned) but the effusion method is recommended when it is necessary to obtain only approximate results. Apparatus for the effusion method, however, is less expensive, and can be assembled at most chemical laboratories. The method combines rapidity with ease of manipulation and a fair degree of accuracy.

4. Below are given some precautions and recommendations regarding the effusion apparatus when using water for the confining liquid:

a. The apparent gravity should always be corrected for water vapor. It is also advisable to standardize the apparatus by the Direct Weighing Method or Gas Density Balance Method of analysis and then apply the correction factor found to results obtained by the effusion method.

b. Temperature should remain constant throughout the experiment and preferably should not be above 30^{o}C.

c. The time of effusion recommended is 90 to 120 seconds. A shorter time gives too much error in stop watch readings and a longer time requires too much time for making a determination. The time of effusion is governed by the size of bulb, diameter of the orifice, and the specific gravity of the effusing gas. An apparatus with a bulb 50 to 100 cc in volume and with an orifice .2 to .3 mm. in diameter gives the desired results.

d. The inside of the tube should be kept clean to eliminate any unnecessary friction so that the water will drain from the tube.

e. Although good results may be obtained with wide variations of waterhead, it is advisable to sue as small a water-head as possible for the start and a water-head of about 1 inch for the finish.

f. The orifice used should be smooth, round and free from burrs. Though an orifice of this type will not necessarily show any appreciable difference in results from an irregular orifice it will give more consistent results.

g. Determinations with the method should preferably be made in a place free from drafts.

5. The method of using mercury as the confining liquid is very satisfactory and gives results which are quite comparable to the tru gravity of the gas if an automatic timing device with which the time can be measured to approximately .05 seconds, be used. The accuracy of the method is .3 to .5 percent.