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CRITICAL STUDY OF THE DETERMINATION OF ETHANE BY COMBUSTION OVER PLATINUM IN THE PRESENCE OF EXCESS OXYGEN

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ABSTRACT

A sample of ethane of known purity was analyzed by the usual slow-combustion method; that is, over a hot platinum spiral in the presence of excess oxygen. The contraction after burning, the carbon dioxide produced, and the oxygen consumed were measured. The average results obtained from a series of 18 determinations indicated the impossibility of attaining the accuracies usually reported in the literature. The average volumetric equation for the reaction was $C_2H_6+3.5116\ O_2=1.9940\ CO_2+2.5190$ contraction. The weighted average equation was $C_2H_6+3.513\ O_2=1.994\ CO_2+2.520$ contraction. The contraction and oxygen consumed were invariably too high, and the carbon dioxide produced was invariably too low. The ethane was calculated from contraction, carbon dioxide, and oxygen separately and in various combinations, both uncorrected and corrected for deviations from theoretical molecular volumes. The average results from different methods of calculation varied from 99.13 percent to 100.76 percent. The best average value found by use of a single formula was 100.11 percent, and resulted from combining the contraction and carbon dioxide as one factor of an equation of which the other factor was oxygen. Such an equation eliminates part of the uncertainty concerning the proper method of correcting for deviation from theoretical molecular volumes. The averages of two pairs of formulas gave results very close to 100 percent. The ethane was also calculated on the assumption that methane, or propane, (known to be absent) was present. (The usual analysis would have been reported as methane and ethane.) Hydrocarbons other than ethane indicated by various methods of calculation from the average of the observed results varied from 0.3 percent of propane to 9.4 percent of methane.

A number of sources of error are discussed. These include small measured losses of ethane and carbon dioxide in the distributor, and a small loss of carbon dioxide by solution in the water produced by the combustion and otherwise present. Such errors must be present in every apparatus of this type, and will effect the analysis of all hydrocarbons to some extent. The observed results may be explained by correcting for these errors, and for the known deviation of carbon dioxide from its theoretical molecular volume with a similar correction for ethane, which is somewhat higher than the best estimated value available.

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I. INTRODUCTION

The direct method of attack in studying the real worth of any method of gas analysis is to use as the basic point of departure a gas of known purity. With such a material at command, the final destination is clear enough. If all the rules are observed en route, and the gas was definitely known at the start, the analytical results obtained are a measure of the value of the method. Unfortunately, no standard gas samples are available to the gas analyst, and perhaps this constitutes the only good reason why the obvious procedure has seldom been employed.

In the present work ethane of known purity was determined by combustion over heated platinum in the presence of excess oxygen. This established method is one of the most widely used in volumetric gas analysis. The accuracies which may be expected from it under the most favorable conditions of operation were thus determined directly for ethane. The errors which may explain the observed deviations from the theoretical result were of such a nature that they will affect the analysis of any hydrocarbon to some extent.

II. PURITY OF THE ETHANE USED

The ethane used in this series of determinations was a fraction separated from a West Virginia natural gas by the prolonged operation of a large rectifying column. It was stored in a 100-cubic-foot cylinder. The sample used for the determinations reported was drawn from the cylinder over mercury into a glass container. Air was excluded by flushing the sampling line with mercury, followed by a prolonged flushing with the sample, which in turn was transferred under measured positive pressure.

The purity of the ethane was studied in two ways: (1) by determining the ratio of carbon to hydrogen, and (2) by the differential vapor pressure method.

1. RATIO OF CARBON TO HYDROGEN

F. D. Rossini, of this Bureau, determined the ratio of carbon to hydrogen according to the method he employed for the methane used in his determination of the heat of combustion of this gas.[1] He reports these ratios as moles of hydrogen per 1.5 times the number of moles of carbon (or moles of water per 1.5 times the number of moles of carbon dioxide in the products of combustion) so that the ratio = 1 for pure C_2H_6. The values obtained are given (as reported) in table 1.

TABLE 1.—*Ratio of hydrogen to carbon in ethane used*

Date	Approximate amount burned (mole C_2H_6)	Mole H_2O per 1.5 moles CO_2	Mole H_2O/1.5 (moles CO_2) corrected for CO produced
Oct. 27, 1932	0.0675	1.00030	1.00010 } average, 1.0000±0.0002.
Oct. 29, 1932	.070	1.00002	0.99982 }
Dec. 2, 1932	.0284	.99944	0.99924 } average, 0.9993±0.0002.
Dec. 9, 1932	.049	.99955	0.99935 }

[1] F. D. Rossini, B.S. Jour. Research, vol. 6 (RP260), p. 37, 1931.

The ratios of the first series indicate pure ethane. The ratios of the second series indicate a change in composition which might be explained by a change in equilibrium between vapor and liquid phases within the storage cylinder. The impurity indicated could not be methane, but might be propane to the extent of 0.42 percent or ethylene to the extent of 0.21 percent. The method of establishing ratios of carbon to hydrogen takes no account of nitrogen or air.

2. DETERMINATION OF PURITY BY THE DIFFERENTIAL VAPOR PRESSURE METHOD

The sample used in the present work was drawn from the cylinder after the second series of the determinations of the ratio of carbon to hydrogen. Its purity was tested by the differential vapor pressure method previously suggested.[2] The vapor pressure of an initial distillate from the liquefied sample was compared with that of a middle cut and also against that of the final residue. The data are as follows: Approximately 1 liter of the sample was condensed at −190.3° C. The pressure above this condensate was 1.5 mm. The temperature was raised to −150° C.; the corresponding pressure was 7.5 mm. The condensate was distilled isothermally at this temperature until a few drops of distillate had collected at −190° C. on one side of the differential manometer, which was then closed. The distillation was continued until approximately half of the original condensate had vaporized; this portion was removed by a mercury vapor pump. The distillation was then continued until a few drops of distillate had collected at −190° C. in the opposite side of the differential manometer. The 2 condensation bulbs of the manometer were surrounded with frozen mercury to insure uniformity of temperature within both bulbs. The pressure of the initial distillate was observed to be 2.02 ± 0.03 mm greater than that of the middle fraction at a temperature of −190.3° C. The middle fraction was removed from the manometer and the distillation again continued until only a few drops of final residue remained. This residue was condensed in the side of the differential manometer previously containing the middle cut. The pressure of the initial distillate was observed to be 2.05 ± 0.03 mm greater than that of the final residue.

The conclusions are: (1) The sample of ethane contained a lower boiling impurity; (2) the sample contained no higher boiling impurity. (There are no known constant boiling mixtures which may have been involved.)

When the source and method of storing the sample are considered, the lower boiling impurities which may be expected, listed in the order of likelihood of occurrence, are methane or nitrogen or air, ethylene or helium. The latter two are not very likely to occur. If methane or ethylene were present in significant amounts, it would be possible to isolate fractions containing them by isothermal fractional distillation [2] of the condensate from which nitrogen had been removed. Accordingly, several days were devoted to a careful separation of a sample of the ethane, employing temperatures of −150° C. at the start and −170° C. at the end of the series of distillations. No increase of vapor pressure at corresponding temperatures

[2] Martin Shepherd, B.S. Jour. Research, vol. 2 (RP75), pp. 1156–7, and 1169–70, 1929.

was observed during these separations. It is accordingly safe to assume that lower boiling hydrocarbons were absent, or present in amounts so small as to be insignificant.

These observations indicate nitrogen or air as the most probable impurity. Assuming that nitrogen was present, we can make a rough calculation of the amount by using an equation derived by Washburn[3] from the laws of Raoult, Henry, and Dalton. If p_2 is the equilibrium pressure when the system is composed of a negligibly small quantity of vapor and a large quantity of liquid, p_1 the equilibrium pressure when the system is composed of a (negligibly) small quantity of liquid and a large quantity of vapor, K_B the Henry's law constant for the impurity B, and $\Delta = p_2 - p_1$, then X_B, the mole fraction of B in the mixture is given by the equation

$$X_B = \frac{K_B \Delta}{(p_2 - K_B)^2 + \Delta(2K_B - p_2)}.$$

In the present case, Δ has been directly measured by the differential manometer, and equals 2.02 mm. If the mixture is assumed to be an ideal solution, $K_B = p^\circ_B$, the vapor pressure of pure B (nitrogen), which is known to be close to 1370 mm at $-190°$ C. The value of p_2 need be known only roughly, and may be assumed to be 1.5 mm, the initial pressure upon condensation. Substituting these values in the above equation, and dropping factors of no significance,

$$X_B = \frac{2(1370)}{(1370)^2 + 2(2 \times 1370)} = 0.0015.$$

This figure would normally represent the mole fraction of nitrogen present in the total mixture, but in this instance the significance is different, since the initial condensate was actually obtained from a separation by distillation and not by a simple isothermal condensation. (This also accounts for the fact that Δ is greater than p_2.) If the separation was complete, it would follow that 0.0015 is the mole fraction of nitrogen in the initial distillate, and not in the entire mixture. Since the difference in purity between the initial distillate and the middle cut was the same as that between the initial distillate and the final residue, it is established that the separation of nitrogen was completed sometime before the middle cut was reached, and the maximum possible amount of nitrogen in the total mixture would be correspondingly reduced to approximately 0.0007. Furthermore, it is possible to compute the difference in purity between any two fractions. If p°_A and p°_B are the vapor pressures of the substances A and B in their pure states, and Δp is the difference in the vapor pressures of the two fractions or distillates, then the difference in purity, Δx_B, is given by the expression

$$\Delta x_B = \frac{\Delta p}{p^\circ_B - p^\circ_A}.$$

In the present case p°_A is negligible (<0.1) and $\Delta\ p$ and p°_B have been measured or are known as noted before

$$\Delta X_B = \frac{2}{1370} = 0.0015$$

[3] E. W. Washburn, Constancy of Pressure During Isothermal Condensation or Vaporization as a Criterion for Purity, Zs. f. physik. Chem., Cohen Festband, p. 592, 1927.

This value checks the former computation of X_B for the mixture, and indicates that the separation of N_2 was completed with the initial distillation. Therefore 0.0015 mole fraction of nitrogen was present in the initial distillate alone. The order of magnitude of the nitrogen impurity may be calculated for the whole sample by assuming that the initial distillate did not comprise more than 10 percent of the total mixture. This assumption is more than safe, since only a few drops were observed from a total mixture of over 2 ml. Since the total volume of the gas sample was close to 1000 ml, the nitrogen impurity (using the above assumption) was $\frac{0.15}{1000}=0.015$ percent or less.

3. ABSORPTION IN ALKALINE PYROGALLOL SOLUTION

The sample showed no measurable contraction after contact with potassium hydroxide solution or alkaline pyrogallol solution.

The conclusion is that the ethane used may be considered as pure for the purpose of this study. If the results of the analyses do not so indicate, the value of the analytical method has been measured. Since the analyses were performed carefully, and since both the apparatus and technic employed would eliminate many of the common errors often present in this general field of gas analysis, it is believed that the results are about as good as can be expected from the slow combustion of ethane.

III. APPARATUS AND METHOD OF ANALYSIS

1. APPARATUS

The standard apparatus for volumetric gas analysis previously described [4] was used. During part of the work, a U-tube of approximately 4 mm bore and 250 mm length was connected to the first 2 stopcocks of the distributor. This U-tube was filled with fresh ascarite and replaced the regular pipette containing potassium hydroxide solution. A water jacket surrounded the U-tube, and the temperature of the water was observed and compared with that of the water surrounding the burette. These observations were made during each measurement of a gas volume, and, together with the known capacity of the U-tube, served as a check against volumetric error from this source.

2. METHOD OF ANALYSIS

The analytical procedure was as follows. From 30 to 70 ml of nitrogen, obtained from the pipette containing alkaline pyrogallol solution, was measured and stored in the "pyro pipette", leaving the manometer and distributor filled with nitrogen and balanced at the pressure of the compensator. Approximately 90 ml of oxygen containing a known small percentage (0.76) of nitrogen was transferred to the burette, measured, and passed to the combustion pipette leaving the manometer balanced. A sample of approximately 20 ml of ethane was taken into the burette and measured. The gas over the mercury in the arm of the manometer connected to the distributor was taken into the burette. The pressures in the burette and combustion tube were independently adjusted to atmospheric. A

[4] Martin Shepherd, B.S.Jour. Research, vol. 6 (RP266), p. 121, 1931.

measured current was passed through the platinum spiral within the combustion pipette. (The spiral was maintained at bright yellow during the combustion.) The burette and combustion tube were connected, and the control stopcock of the burette opened to the constriction with the mercury reservoir connected thereto placed above the top of the burette. In this manner the gas was passed very slowly from the burette into the combustion pipette. The first passage usually required between 15 and 20 minutes. This insured the continued presence of excess oxygen around the combustion spiral, and prevented thermal decomposition of the ethane (which occurs when the sample is passed into the combustion pipette at the rates normally specified in the literature). After the first prolonged passage, 4 additional passages were made at rates varying from 5 to 3 minutes. The residual gas was measured and the total contraction upon burning was thus determined.

At this point the procedure took one of two courses, depending upon the method used for determining the carbon dioxide produced by the combustion.

When the regular method was employed, the procedure was as follows: Gas contained in the arm of the manometer connected to the compensator was taken into the burette, whence it was passed, together with the residue from combustion, into the pipette containing potassium hydroxide solution. The measured portion of nitrogen was transferred from storage in the "pyro pipette" to the burette and thence to the "KOH pipette." After returning the combined gases from the KOH pipette, 2 more passages into this pipette were made, followed by 1 passage into the combustion pipette (to regain carbon dioxide from that section of the distributor), and finally 2 passages into the KOH pipette. The residual gas was measured, establishing the amount of carbon dioxide formed during the combustion. Gas from the manometer was again taken into the burette and, together with the residue remaining after the absorption of carbon dioxide, was passed three times into the pyro pipette, once into the KOH pipette, once into the combustion pipette (thus regaining oxygen from these parts of the distributor), and finally twice into the pyro pipette. The residue from this absorption was measured and the excess oxygen determined. The oxygen consumed during the combustion was thus determined, as was the nitrogen (if any) in the original sample.

When the carbon dioxide was determined by absorption on ascarite, the procedure following the combustion was altered. After displacing the gas from the manometer, the residue from the combustion was passed slowly through the ascarite U-tube into the combustion pipette. The stored nitrogen was added as before, and the combined gases passed directly from the combustion pipette to the burette, by-passing the ascarite tube. This method of routing the gases was followed regularly. Repeating this procedure five times was sufficient to flush all of the carbon dioxide from the distributor connections and collect it in the ascarite. Completeness of absorption was determined by repeating the procedure. After thus determining the carbon dioxide produced during the combustion, the excess oxygen was obtained by 4 passages through the ascarite tube to the pyro pipette, 1 (with ascarite by-passed) to the combustion pipette, and 2 final

passages to the pyro pipette. Completeness of absorption was determined as before. All gas volumes were measured with the ascarite tube connected as part of the distributor when the pressure was finally balanced.

The removal of carbon idoxide by a dry reagent was resorted to in order to eliminate, so far as possible, the errors arising from changes in the amounts of gases dissolved in the potassium hydroxide solution. The alkaline pyrogallol solution is in contact with nitrogen alone after the absorption of oxygen, and the chances of error caused by a change in the amount of nitrogen dissolved are not so great as may be encountered with the potassium hydroxide solution. This solution is in contact with mixtures of oxygen and nitrogen of varying composition, and it is not impossible to lose or gain small but sometimes significant amounts of oxygen during the absorption of carbon dioxide. Furthermore, since it is necessary to pass the gas after the absorption of oxygen into the KOH pipette in order to regain oxygen kept in this part of the distributor after the absorption of carbon dioxide, the danger of displacing oxygen from the potassium-hydroxide solution and changing the volume of excess oxygen is not negligible, since nitrogen may also be exchanged in this process.

The first five of the determinations reported were made using the wet reagent for the removal of carbon dioxide, while the dry reagent was used for the rest. The differences obtained between the two procedures are small and will not be discussed further in the present paper. A later report will deal with this type of error, as it may occur in usual practice.

IV. ANALYTICAL RESULTS

The data obtained will be represented as follows: S, volume of the sample; TC, contraction after burning ("total contraction"); CO_2, volume of carbon dioxide produced; O_2, volume of oxygen consumed; N_2, volume of nitrogen in sample (if any). The same symbols will be used to identify numbers representing relative volumes in a volumetric equation.

If the reaction

$$C_2H_6 + 3.5\ O_2 = 2CO_2 + 3H_2O$$

is complete and the only reaction which takes place, if the gases measured were all ideal gases, and if there were no errors of manipulation or observation and no gains or losses through solution or otherwise except during the absorption of a constituent in the reagent intended for it, the volumes observed would correspond exactly to the following equation:

$$\begin{array}{lllll} C_2H_6 + 3.5\ O_2 = & 2CO_2 + & 2.5\ TC. & & (1) \\ 1\ \text{vol.} \quad 3.5\ \text{vol.} & 2\ \text{vol.} & 2.5\ \text{vol.} & & \end{array}$$

The observed volumes did not correspond exactly to this simple equation, and the remainder of this paper will be devoted to a discussion of some of the probable reasons why they did not correspond, and of the results of assuming that they did. The last assumption is, of course, the one usually made in reporting analyses.

The results of 18 analyses of the pure ethane are shown in table 2. The observed values of each of the three important quantities $\frac{TC}{S}$, $\frac{CO_2}{S}$, and $\frac{O_2}{S}$ were plotted, and a selection made of what appeared to be the best average value, which was slightly different from the arithmetical average of all observations, since in each case a small number of extreme values appeared to be the result of accident or inaccurate observation. An equation in which these averages are used,

$$C_2H_6+3.513\ O_2=1.994\ CO_2+2.520\ TC, \qquad (2)$$

is believed to represent, as well as any that could be chosen from the observed data, the deviations from the ideal conditions (represented by equation 1) which are inherent in the process and not the result of random error.

TABLE 2.—*Observed results of 18 determinations of ethane*

[For an explanation of the symbols used consult the text, p. 789]

Analysis no.	$\frac{(TC)}{S}$	$\frac{(CO_2)}{S}$	$\frac{(O_2)}{S}$	Carbon dioxide in products of combustion	$\frac{N_2}{(ml.)}$
				Percent	
1	2.5201	1.9846	3.5080	74.1	+.07
2	2.5168	1.9959	3.5120	76.5	−.01
3	2.5207	1.9965	3.5148	67.1	−.05
4	2.5200	1.9968	3.5145	66.1	−.05
5	2.5117	1.9918	3.5015	70.9	−.04
6	2.5191	1.9944	3.5041	64.9	−.18
7	2.5179	1.9930	3.5103	67.5	−.01
8	2.5169	1.9903	3.5033	69.5	−.08
9	2.5238	1.9937	3.5133	67.8	−.08
10	2.5109	1.9904	3.5014	71.3	.00
11	2.5156	1.9911	3.5179	78.8	+.12
12	2.5242	1.9949	3.5106	86.9	−.06
13	2.5204	1.9950	3.5149	71.4	−.01
14	2.5171	1.9990	3.5132	63.9	−.06
15	2.5203	1.9995	3.5170	72.4	+.08
16	2.5205	1.9915	3.5158	68.3	−.10
17	2.5223	1.9962	3.5139	66.2	−.01
18	2.5228	1.9972	3.5197	67.8	----------
Arithmetical average	2.5190	1.9940	3.5116	70.6	−.03
Selected average	2.520	1.994	3.513	----------	----------
Probable systematic error	±0.003	±0.003	±0.003	----------	----------

If ethane is known to be the only combustible compound present, the amount can be computed from the oxygen burned, the carbon dioxide formed, or the contraction, or from various combinations of these quantities. Most gas analyses are computed on the assumption that the ideal volumetric relationships will prevail as represented by equation 1. If this assumption were correct, all the methods of calculation would give identical results whatever the purity of the sample, and with ethane of the purity of that used, the common result should have been 100 percent.

TABLE 3.—*Results of computing ethane from average observed data by the use of various formulas*

[In each case the formula stated multiplied by 100 gives the percentage of ethane]

No.	Formula	Ethane found
		Percent
1	$TC/2.5S$	100.80±0.12
2	$CO_2/2S$	99.70± .15
3	$O_2/3.5S$	100.37± .08
4	$(TC+CO_2)/4.5S$	100.31± .1
5	$(TC+CO_2-O_2)/S$	100.10± .3
6	$[CO_2/2S+(TC+CO_2)/4.5S]/2$	100.00± .15
7	$(CO_2/2S+O_2/3.5S)/2$	100.04± .2

The results of computing ethane by various formulas are shown in table 3. In each case the selected average of the observed values for $\frac{TC}{S}$, $\frac{CO_2}{S}$, and $\frac{O_2}{S}$ given at the bottom of table 1 was used to compute the most probable result.

The indicated uncertainty in the result was estimated, as before, by plotting the percentages of ethane computed from each of the 18 analyses and disregarding a few extreme results believed to be certainly the result of random errors.

By the use of the first three formulas the percentage of ethane is, of course, simply computed from the three quantities which are independently observed during the analysis. Formula 4 has the merit of eliminating the effect of any error in the measurement of the products of combustion before the absorption of carbon dioxide, of deviations of carbon dioxide from the simple gas laws and of any loss, by solubility or otherwise, of carbon dioxide before the final absorption. This is true because any error in this part of the analysis affects the total contraction and the carbon dioxide to equal and opposite extents. Formula 5 has the merit of simplicity of computation and in this case appears to give a good result. However, the effect of any loss of oxygen during the course of the analysis (by oxidation of metals or previously deposited carbon in the pipette, or solution in the distributor or in the reagent for carbon dioxide, etc.) is seven times as great as when the ethane is computed from formula 3. This probably accounts for the relatively great scattering of results computed with this formula. Because formula 2 gives results that are consistently too low and formula 4 results that are consistently too high by almost exactly the same amount, the temptation to average the results of the two (formula 6) could not be resisted. The same fortuitous relationship exists between formulas 2 and 3 (formula 7).

When it is not known that ethane is the only hydrocarbon present, the amounts of two hydrocarbons, ethane and methane or ethane and propane, can be computed from any two of the three quantities which are independently observed in the analysis, or from one of these quantities and a combination of the other two. Again, ideal reactions, obedience to the simple gas laws, and correct observation would result in exact agreement among the results of analysis computed by different methods, whatever the hydrocarbons present; and in the case of the pure ethane, the amount of ethane found would be 100 percent. In table 4 are the results of computing ethane and methane

or ethane and propane from each of the three possible pairs of observed quantities and from the oxygen consumed and the sum of carbon dioxide and total contraction. The latter method (formula 11) possesses the merits mentioned in connection with the computation of ethane alone from the sum of the carbon dioxide and the total contraction, and is the only combination of the three observed quantities which seems worth using in computation. The combination used in normal practice (9) is apparently worthless.

A negative percentage of methane, computed from any formula, indicates an equal positive percentage of propane; the analysis should then be recomputed in terms of ethane and propane. If a negative quantity of propane is indicated, the situation is, of course, reversed. Computation from the average values for any pair of the observed quantities indicates the presence of methane; computation from the fourth formula (11) indicates the presence of propane rather than methane.

TABLE 4.—*Results of computing ethane and methane or ethane and propane from average observed data by the use of various formulas*

[In each case the formula stated, multiplied by 100 gives the percentage of the hydrocarbon]

No.	Constituent	Formula	Hydrocarbons found			
			C_2H_6	CH_4	C_3H_8	Total
			Percent	*Percent*	*Percent*	*Percent*
8	Ethane	$(4CO_2-2O_2)/S$	95.0			
	Methane	$(4O_2-7CO_2)/S$		9.4		104.4
9	Ethane	$(4CO_2-2TC)/3S$	97.9			
	Methane	$(4TC-5CO_2)/3S$		3.7		101.6
10	Ethane	$(O_2-TC)/S$	99.3			
	Methane	$(7TC-5O_2)/4S$		1.9		101.2
11	Ethane	$[10(TC+CO_2)-12O_2]/3S$	99.8			
	Propane	$[9O_2-7(TC+CO_2)]/3S$			0.3	100.1

The wide divergence from correct values of the results of computations in which the amount of carbon dioxide produced by combustion is involved seems to indicate that this introduces too great a total error. Its elimination by means of formula 11 appears desirable if analyses are to be computed without correction for deviations from the simple gas laws or other conditions which may be known to affect the result. This formula possesses the merit of relieving the chagrin of the analyst who obtains such total percentages as 101 to 104.

V. PROBABLE SOURCES OF ERROR

No attempt will be made here to make a complete list of all the possible sources of error attending the usual volumetric gas analysis. However, the deviations of the observed data from those which would be necessary to correspond to the ideal equation (1) are too large and too systematic to be attributed entirely to accidental or random errors. They must have resulted in part, at least, from conditions which recur in every analysis. Some of the more probable and important of these will now be discussed.

1. ERRORS CAUSED BY THE DEVIATIONS OF ETHANE AND CARBON DIOXIDE FROM IDEALITY

First in apparent importance is the fact that ethane is not an ideal gas but that a given weight (or given number of moles) of it occupies less space than corresponds to Avogadro's law. Unfortunately, completely reliable data for estimating this deviation are lacking, but from the best information available it appears that a given quantity of ethane will occupy, at atmospheric pressure and average laboratory temperature, only 0.990 of the volume computed from its molecular weight and the assumption that it is an ideal gas.

We must next consider that carbon dioxide is not a perfect gas. At atmospheric pressure and laboratory temperature the volume of carbon dioxide is about 0.994 of that of an ideal gas. If the pressure is lowered, the deviation from the ideal becomes less and approaches zero as the pressure approaches zero. The problem is complicated by the fact that the molecular volume is without doubt affected by other substances present. However, this effect is probably so small that it will be within the limit of possible accuracy of the analysis to assume the deviation of carbon dioxide from its theoretical molecular volume to be proportional to its partial pressure in a mixture. The percentage of carbon dioxide in the mixtures in which it was measured during the analyses averaged 70. Making the correction corresponding to the assumption stated, and also the correction for the deviation of ethane, the volumetric relationship, instead of being represented by equation 2, should be represented by the equation

$$0.990\ C_2H_6 + 3.5\ O_2 = 2\ (0.9958)\ CO_2 + 2.498\ TC \qquad (3)$$

which reduces to

$$C_2H_6 + 3.535\ O_2 = 2.012\ CO_2 + 2.523\ TC \qquad (4)$$

This does not correspond to the observed facts.

This disagreement with the observed facts is worth a moment's reflection on the part of the gas analyst. The reason for this is that, while most gas analyses are computed from the ideal volumetric equations, the present tendency to correct such results (if any correction is made) is based upon the assumption that the only existing error is that caused by the deviations of the imperfect gases from their theoretical molecular volumes. Since this more dignified effort has been accepted as an entirely sufficient corrective, it appears worth while to make a direct comparison of the results obtained from the ideal equations with those obtained from the same equations corrected for deviations of ethane and carbon dioxide from ideality. Such a comparison is made in table 5. It will be seen that corrections for the deviations of these gases do not remedy the situation, and in some cases the corrected equation leads to even greater errors than are obtained from the uncorrected equation. It is obvious that other errors, such as those discussed in the following section, must be considered.

TABLE 5.—*Comparison of the results obtained from formulas derived from the ideal volumetric equations with those obtained from the same formulas corrected for the deviations of ethane and carbon dioxide from their theoretical molecular volumes*

Formula (multiply by 100 to obtain percentages)	Percentages obtained from the ideal gas equations (arithmetical average of 18 analyses)		Percentages obtained from the ideal gas equations corrected for the deviations of C_2H_6 and CO_2 from their theoretical molecular volumes	
	C_2H_6	CH_4	C_2H_6	CH_4
TC/2.5S	100.76		99.81	
CO_2/2S	99.70		99.13	
O_2/3.5S	100.33		99.32	
(4TC−5CO_2)/3S	97.93		98.00	
(4CO_2−2TC)/3S		3.55		2.28

2. ERRORS CAUSED BY LOSSES OF ETHANE AND CARBON DIOXIDE DURING THE ANALYSIS

Next, consider the loss of carbon dioxide which occurs during a combustion. This may happen in 3 ways, and as a consequence may make the observed CO_2 too low and TC too high by a corresponding amount. The 3 avenues offered for escape of carbon dioxide are:

(1) Solution in the water formed during combustion. This water is condensed in the presence of the carbon dioxide formed during combustion and will, hence, be saturated. At the laboratory temperatures observed during these analyses, water will dissolve about 0.8 of its own volume of pure carbon dioxide. Since the effect is proportional to the concentration of the carbon dioxide (0.70 in this case), and since the average amount of water produced by a single combustion was about 0.05 ml, the amount of carbon dioxide lost should be approximately 0.04 ml.

(2) Solution in the other water present in the apparatus. This includes both the water present in the burette and the condensate from previous combustions which collects in the combustion pipette. The latter is not allowed to accumulate beyond a volume of about 0.2 ml. Furthermore, it may be assumed to be in substantial equilibrium with carbon dioxide. On the other hand, the water on the burette walls is taken fresh at the start of each analysis. It is present as a film or in small droplets. The total amount present is small but varies somewhat with the condition of the burette wall. There is never enough present to obscure the mercury meniscus, although there may be as much as 0.05 ml on the glass wall, as determined by actual observation. Just how much carbon dioxide will be dissolved is not known, nor could any fixed correction be derived. However, the correction would be small and the actual variation would not be great.

(3) Solution in the rubber connections of the distributor or manifold. There are 3 of these involved, 2 of which the carbon dioxide must pass on its way back from the combustion pipette. These connections are formed by butting together glass capillaries which are ground flat at the ends in order to present a minimum of surface to the rubber

tubing, and the rubber sleeve itself is secured at both sides by several turns of waxed dental floss. Blank analyses established the fact that approximately 0.05 ml of pure carbon dioxide was lost in the distributor of the apparatus during the average time of contact for a combustion. If the loss is proportional to the average concentration of carbon dioxide in the products of combustion, about 0.04 ml could be accounted for.

The order of magnitude of the error representing the entire loss of carbon dioxide during combustion should, therefore, be at least 0.08 ml.

Equation (4) corrected for this loss becomes

$$C_2H_6 + 3.535\ O_2 = 2.008\ CO_2 + 2.527\ TC \qquad (5)$$

A similar correction should be made for the observed solubility of ethane in the stopcock lubricant and rubber connections. The pure sample is in contact with 2 of the rubber connections previously described for about 20 minutes during its passage to the combustion pipette. Blank analyses established the order of magnitude of the loss of ethane as about 0.06 ml. The loss of ethane, propane and butane were measured in the distributor of the apparatus and also in a rubber tubing of 10 cm length. In the case of butane, the loss was considerable in the distributor and furthermore it was possible to regain some dissolved butane by passing another gas, e.g., nitrogen, through the distributor. Ethane should behave in a smilar manner, so that it would be possible to lose a small portion of the sample at the beginning of the analysis and regain an indeterminate amount later on. This behavior makes a blank correction difficult, even if all other circumstances were identical for each analysis. The fresh nitrogen balance obtained for each analysis would prevent the ethane from reaching any saturation equilibrium in the distributor, and no constant error could be expected from this source, although it might be a constantly present one.

This makes a definite correction for ethane somewhat uncertain, although the need of one is clearly indicated.

On comparing equation (5) with equation (2) it is apparent that the "corrected" values for oxygen consumed, carbon dioxide produced and total contraction are all too high to agree with the observed results. If some ethane was lost by solution or otherwise before combustion, the corrected equation can be brought into better agreement with the observed results. The deficiency of ethane to be accounted for is greater than the amount lost during blank analyses. However, if the latter loss is assumed to be substantially correct, and equation 5 is corrected accordingly, the equation.

$$C_2H_6 + 3.525\ O_2 = 2.002\ CO_2 + 2.520\ TC \qquad (6)$$

is obtained.

If the rather uncertain correction for the deviation of ethane from Avogadro's law as too great, the "corrected" results might be brought into good agreement with those actually observed. It is interesting to assume this, if merely for the sake of ascertaining how far the original value of 0.990 assumed for the deviation of ethane would have to be altered. If such arithmetical thaumaturgy is in-

voked to the extent of transforming the ethane correction to 0.993, equation (6) becomes

$$C_2H_6+3.515\ O_2=1.995\ CO_2+2.516\ TC, \tag{7}$$

which represents the observed data,

$$C_2H_6+3.513\ O_2=1.994\ CO_2+2.520\ TC, \tag{2}$$

in most respects.

3. ERROR IN THE RESIDUAL NITROGEN

At the end of each analysis the residual nitrogen was measured. Usually it did not have exactly the volume taken at the start to fill the distributor and the upper part of the compensator. In the 18 analyses the differences represented an average loss of 0.03 ml, but these differences were erratic, except for the fact that a loss was observed in 13 out of 18 cases. However, 0.03 ml is within the probable error. It was thought possible that the loss of nitrogen was caused by oxidation, but a test of the water, produced during several combustions, by the standard method employed in water analysis showed no trace of nitrates.[5] A number of blank tests were made by passing over the hot wire both air and mixtures of oxygen with the approximate amount of nitrogen present in the manometer and distributor. Small contractions were observed, but no assurance was obtained that an error of definite magnitude had been discovered.

Further evidence tending to support the belief that no loss of nitrogen occurred by oxidation was obtained as follows. Approximately 28 liters of air was passed over a heated platinum spiral and the exit gas was passed through a solution of potassium hydroxide. The rate of passage was approximately 20 ml per minute and the temperature of the wire closely duplicated that of the analyses. The platinum spiral was three times the length of the one used in the analyses, and was suspended in a tube of 5-mm bore so that intimate contact with the air stream was insured. The potassium hydroxide solution was examined for nitrates or nitrites, by reducing with Devarda's metal and testing for ammonia with Nessler's reagent. The test indicated that the amount of nitrogen lost could not have been as great as 0.001 ml. per 100 ml of air.

In view of these facts, no correction was attempted. The possibility of a small error of this nature still remains, however, since the oxidation of nitrogen may have occurred during the actual combustion of ethane to a greater extent than indicated by tests with air.

VI. CONCLUSION

In having thus indicated probable sources of error that account for most of the discrepancy between the ideal equation and the average of the observed results, it must not be assumed that the corrections offered are necessarily always of the right magnitude or that other sources of error do not exist. The purpose of this paper will be accomplished if attention is generally directed to three facts: (1) that analyses of hydrocarbons computed from the ideal equation

[5] Notes on Practical Water Analysis, by W. D. Collins, U.S. Geol. Survey Water Supply Paper no. 596-H, 241, 1928. The analyses were made by E. Wichers and F. W. Schwab of the Bureau of Standards.

should not be regarded as necessarily accurate, no matter how carefully the work is done; (2) that corrections for deviations from ideality of the imperfect gases are not always sufficient to eliminate the inaccuracy; and (3) that there are numerous minor sources of error for which it may or may not be possible to make satisfactory corrections.

While the sources of error which have been considered do not afford the complete or, necessarily, the entirely correct explanation of the facts observed, the facts themselves do offer an empirical solution to the problem of computing the analysis of ethane. As far as the present work is concerned, formulas derived from the observed volumetric equation (2)

$$C_2H_6+3.513\ O_2=1.994\ CO_2+2.520\ TC$$

would give considerably more accurate results than could be obtained from the established formulas in general use. It is interesting to consider the probable extent to which the general application of this equation is justified.

From a study of the nature of some of the errors which are known to have been present, it is apparent that the actual values observed depend primarily upon three general factors: 1, the gas examined; 2, the technique employed, and 3, the particular apparatus used. It is obvious that equation (2) cannot be generally useful unless the conditions at hand closely approximate those existing in the present work. First, the general application is at once limited to the analysis of ethane, or mixtures containing very high percentages of ethane and no other combustible gas. Second, a variation of the technique employed might greatly influence the values obtained. However, the one prescribed in this report can be reproduced, perhaps advantageously in some cases. If this is done, equation (2) may retain its general usefulness. Third, the errors caused by losses of ethane and carbon dioxide must be substantially duplicated in any apparatus. It cannot be supposed that this condition will ever be entirely realized. The extent to which these errors will be reproduced in different apparatus is uncertain. However, apparatus of this general type usually include the same number of rubber connections and stopcocks, and it is not unlikely that a fairly average condition was represented in the present work. If this is substantially true, equation (2) may still be considered as fairly suitable for general use. It is at least not inconsistent to suppose that its use would improve the accuracy of such analyses. The safer procedure, of course, would be for the analyst to calibrate his own apparatus and technique by means of a sample of ethane of known purity.

It is proposed to continue the development of empirical volumetric equations of this type for other gases, both pure and in known mixtures, in the effort to improve the accuracy of the slow combustion method.

While it may be possible to substantially improve the accuracy of this method, the data obtained for ethane indicate that highly accurate results cannot be obtained by the usual volumetric procedure. This suggests recourse to gravimetric combusion methods for those cases in which the accuracy demanded may justify a relatively complicated and time consuming procedure.

WASHINGTON, *September 23, 1933.*