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ERRORS IN GAS ANALYSIS ARISING FROM LOSS OF GAS BY SOLUTION IN RUBBER CONNECTIONS AND STOPCOCK LUBRICANT

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ABSTRACT

This paper presents experimental data on the loss, by solution, of certain gases in the rubber connections and stopcock lubricant of volumetric gas-analysis apparatus. It is shown that errors, which may be serious, result whenever high concentrations of carbon dioxide, ethane, ethylene, acetylene, propane, propylene, or butane are present in such apparatus. A method of obtaining an approximate correction by means of a blank analysis is proposed. This correction improves the accuracy of the analysis, but with gases which are very soluble, such as propylene and butane, the results, while improved, are still very unsatisfactory.

CONTENTS

	Page
I. Introduction	353
II. Apparatus	355
III. Experimental procedure	355
IV. Experimental results	357
1. Results of blank analyses with regular apparatus (method 1)	357
2. Results obtained by method 2 (magnified rates of solution)	357
(a) Loss of various gases in rubber tubing	357
(b) Losses of butane with gray-rubber tubing and with lubricants of different composition	358
V. Application to analytical results	359
VI. Conclusion	361

INTRODUCTION

Modern volumetric gas-analysis apparatus is generally of the type which employs a distributor (or manifold) to connect the burette with the various pipettes. For necessary convenience, the separate parts of such apparatus are connected by means of rubber tubing. These connections are made by placing a rubber sleeve over glass capillary tubes, the ends of which are closely butted together. When such a joint is properly made and secured,[1] it may be depended upon to cause no ordinary leakage under the conditions existing during an analysis.[2]

[1] In assembling such connections, the glass capillaries should be ground flat at the ends, so that a minimum surface of rubber is exposed. The rubber sleeve should be secured at both ends by tightly wrapped waxed dental floss.

[2] For example, many repeated routine tests have shown that no measurable leakage occurs when air is contained in the apparatus at pressures both greater and less than atmospheric. Such tests extend over a period exceeding that required for an analysis, and the pressure differences imposed are greater than will occur during an analysis.

It is well known, however, that many gases are soluble in rubber. Some of these gases may be encountered in samples to be analyzed, and one at least—carbon dioxide—occurs regularly during the majority of combustion analyses. In addition, it is known that many gases, particularly the hydrocarbons, are soluble in the greases which are used to lubricate the stopcocks of gas-analysis apparatus.

It has previously been supposed (insofar as ordinary gas analysis is concerned) that no significant amounts of gases would be lost by solution in the small surface of rubber exposed by connections such as those described, or by solution in the lubricant of stopcocks. The purpose of this paper is to report experimental data showing that significant amounts of various gases are lost by such solution, and that the errors caused by such losses are frequently significant and sometimes large.

In order to picture the possibilities involved, a brief outline will be given for the procedure of an ordinary combustion analysis.

1. A volume of oxygen in excess of that required for the proposed reaction is measured in the burette and transferred to the combustion pipette.

2. The sample to be burned is measured in the burette, whence it is passed very slowly into the combustion pipette, and reacts with oxygen in the presence of hot platinum. Thereafter the mixture present is repeatedly passed back and forth between burette and pipette until the reaction is completed. (The volume of the sample is hereafter identified as *S*.)

3. The products of combustion are allowed to cool in the combustion pipette, and are then returned to the burette where the contraction resulting from the reaction is measured. (This volume is hereafter identified by the symbol *TC*.)

4. The volume of carbon dioxide produced by the reaction is then determined. (This is identified as CO_2.)

5. The excess oxygen is then determined, and from this volume of oxygen consumed (O_2) is obtained.

Since the three factors—*TC*, CO_2, and O_2—are used to calculate the nature and amounts of the combustible gases, it is obvious that any loss of gas during any process involved in obtaining these values will cause an error in the computation. Furthermore, the effect of small losses will usually be magnified by the mathematics of the computation.[3]

Step number 2 of the procedure outlined is the one during which such losses are very troublesome. This may happen as follows:

(*a*) If the sample contains a gas which is soluble in lubricant or rubber, significant amounts of this may be lost during its measurement. In some cases, it was found that no reliable measurement could be made, since solution occurred at a rate rapid enough to prevent adjustment of the pressure of the sample to the fixed reference pressure.

(*b*) If the sample contains a gas which is soluble in lubricant or rubber, a significant amount may be lost during the slow passage into the combustion pipette. Some of the gas so lost will never reach the reaction zone. A part of it may reappear when the products of combustion are returned to the burette, with the possibility of burn-

[3] The reader who is not familiar with the general procedure and computation of gas analysis may supplement the general picture given here by referring to any good text on the subject, or to B.S. Research Paper 266.

ing during the later passages into the combustion pipette. Such losses will affect *TC*, CO_2, and O_2.

The problem is somewhat complicated when consideration is given to the actual behavior of the dissolved gases. In general, two things may be expected to occur: 1. When a gas dissolves in the rubber tubing, a portion of it may completely penetrate the tubing and be given up to the air outside of the apparatus. This will produce the same effect, as far as the analysis is concerned, as though actual leakage had occurred during the particular procedure involved. 2. Some of the dissolved gas will remain in the rubber (and lubricant) until a gas of a different composition is brought into contact with the rubber and lubricant within the apparatus. The dissolved gas will then begin to reappear as a contamination, thus changing the volumes and introducing errors.

It is consequently possible to lose some gas altogether, and to lose a gas during one step of the analysis only to regain a portion of it during subsequent steps or subsequent analyses.

(*c*) The carbon dioxide produced during the combustion is in contact with rubber and lubricant at all times after the initial passage of the sample into the combustion pipette, and until it is finally removed in step number 4. Any carbon dioxide lost during this period will affect both *TC* and CO_2.

In order to establish the probable errors caused by such losses, measurements were made of the rate of solution of various gases. These measurements were conducted:

1. In the gas analysis apparatus, as used in general practice.
2. With the distributing train replaced by 8-cm lengths of different rubber tubes. (To magnify the losses caused by rubber connections.)
3. With the distributing train replaced by an 8-cm length of glass tubing coated inside with different lubricants. (To magnify losses caused by lubricated stopcocks.)

II. APPARATUS

The apparatus used in the experiments was that described by Shepherd.[4] The gas comes in contact with two rubber connections when passed between the burette and any pipette. In addition, one rubber connection between the compensating unit and the distributing train is involved to a greater or lesser degree, during the measurement of any gas. Unless otherwise specified the rubber was pure gum, acid cured, with 5-mm bore and 1.75-mm wall.

The stopcock grease employed was made of rubber, vaseline, and paraffin in the manner described by Shepherd and Ledig.[5] The gases used were carbon dioxide, acetylene, ethylene, ethane, propane, propylene, and butane; all were thought to be reasonably pure, but only in the case of the ethane and carbon dioxide was the purity known.

III. EXPERIMENTAL PROCEDURE

Two methods of measurement were employed. The first was to set up a condition in the apparatus approximating that of the usual analytical procedure. The distributing train and manometer were filled with nitrogen at the pressure (nearly atmospheric) at which the

[4] An Improved Apparatus and Method for the Analysis of Gas Mixtures by Combustion and Absorption. Martin Shepherd, B.S. Jour. Research, vol. 6 (RP266), p. 121, 1931.
[5] Ind. Eng. Chem., vol. 10, p. 1059, 1927.

manometer balanced. The sampling leads to the burette were flushed with the gas to be used, and a sample of this gas was taken into the burette under positive pressure. The stopcock at the top of the burette was then closed and the pressure of the gas adjusted to approximately atmospheric. The manometer and burette stopcocks were then opened to connect the manometer and burette. The pressure of the gas in the burette was then adjusted to the fixed pressure of the compensator, and its volume read. This procedure was employed to prevent, as far as possible, the mixing of the sample with the nitrogen in the manometer, thereby minimizing the solution of the sample in the rubber connection between the compensator and distributing train. It is doubtful whether this was entirely successful, but some such method was necessary to obtain the original volume of the sample, particularly in the case of the more soluble gases. The samples taken were always about 20 ml. The stopcocks were then turned so that the gas in the manometer was shut off from the burette and distributor, and the burette was connected by way of the distributor and two rubber connections to the combustion pipette. This moment was taken as zero time and the gas in the burette was immediately started on a slow passage to the combustion pipette. The platinum spiral in the combustion pipette was not heated.

At convenient times over a period of 30 or more minutes the gas in the combustion pipette was returned to the burette and its volume determined. The difference between the original volume at zero time and the volume at any subsequent time is the loss attributed to the solution of the gas in the rubber connections and stopcock lubricant. The data obtained were recorded as elapsed time compared with the corresponding loss of volume.

The procedure described is essentially a blank analysis. A procedure of this general type may be devised for any particular case, so that it will afford corrections to be applied to a corresponding analysis. However, the losses measured were sometimes small, and did not always exceed the limiting accuracy of the volumetric system sufficiently to justify rigid conclusions. Therefore, a second method was employed which purposely magnified the losses previously observed.

The second method employed was to replace the distributing train and combustion pipette by a piece of rubber tube about 8-cm long, or with a piece of glass tubing of the same length coated on the inside with vaseline or other stopcock lubricant. The exit end of the rubber or glass tube terminated in a stopcock so that either could be flushed out at the start of a test with a portion of the sample.

The procedure was to take a sample of about 80 ml into the burette and to flush about 60 ml of it through the stopcock at the end of the tube which replaced the distributing train. After closing this stopcock the volume remaining was determined, observing the same precautions described for the first method. The time at which this initial volume was determined was taken as zero time. At convenient intervals the manometer was rebalanced and the volume at manometer pressure determined. In this manner, data were obtained confirming the smaller (and more difficultly measurable) losses obtained with the combustion pipette and distributing train. The second method is open to the serious objection that at zero time the rubber tube (or lubricant) is partially saturated with gas and consequently the measured losses are lower than otherwise would have been obtained.

IV. EXPERIMENTAL RESULTS

1. RESULTS OF BLANK ANALYSES WITH REGULAR APPARATUS (METHOD 1)

The experimental data obtained by both methods are presented in the form of curves, the ordinates of which are elapsed time in minutes and the abscissas are milliliters of gas lost by solution.

The losses by solution which result when various gases are subjected to the analytical manipulations corresponding to a combustion and the measurement of the resulting contraction are shown in figure 1.

The data do not justify drawing separate curves for the four less soluble gases, i.e., carbon dioxide, acetylene, ethylene, and ethane,

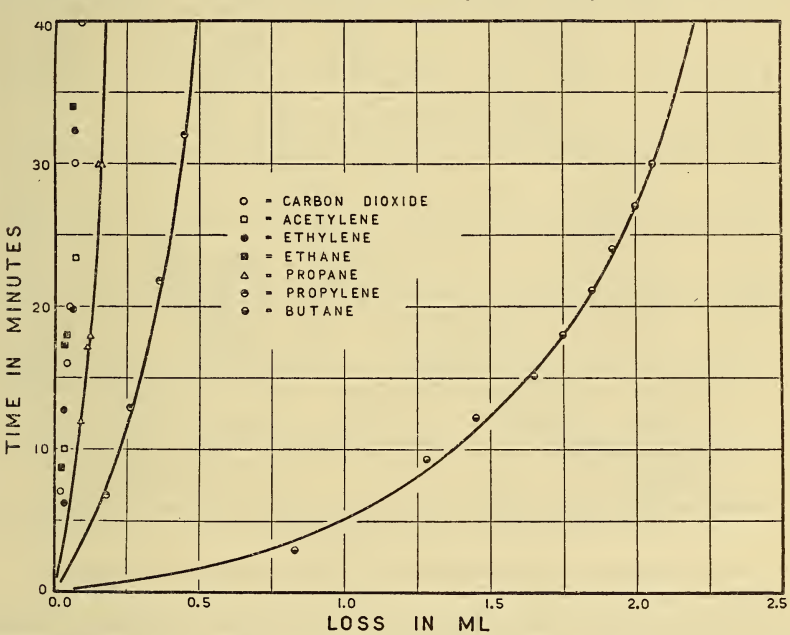

FIGURE 1.—*Loss by solution in the distributor of the gas analysis apparatus.*

and no conclusion may be drawn other than that their rates of solution are of the same order of magnitude. The curves for propane, propylene, and butane are satisfactorily smooth and indicate increasing rates of solution for these gases in the order given. The smoothness of the curves does not, however, justify their use as a direct correction to be applied to analytical results because, as will be shown in figure 2, they represent what may be expected only under the particular set of conditions prevailing when the tests were made.

2. RESULTS OBTAINED BY METHOD 2 (MAGNIFIED RATES OF SOLUTION)

(a) LOSS OF VARIOUS GASES IN RUBBER TUBING

The curves of figure 2 represent the data obtained when the combustion pipette and distributing train were replaced by a piece of clear rubber tubing 8-cm long.

Under these conditions the less soluble gases seem to be separated into two groups, carbon dioxide and ethylene being dissolved less rapidly than acetylene and ethane.

The curves showing the results of attempted duplicate tests for propane and propylene illustrate the change in rate of solution which may be expected with changing experimental conditions (particularly temperature), plus the manipulative error in choosing zero time. In these tests, fresh rubber tubing (of the same length and composition) was used for each determination, and the stopcocks were regreased with fresh lubricant of the same composition previously used.

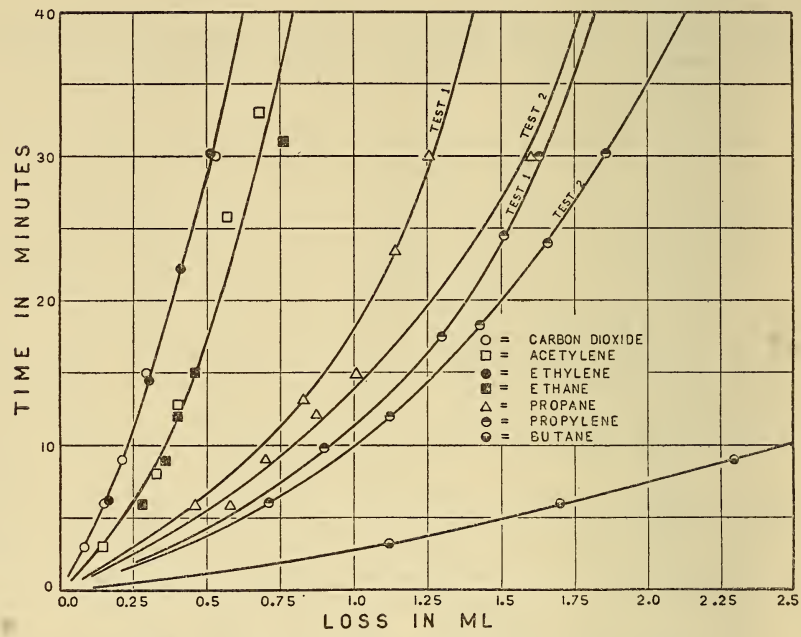

FIGURE 2.—*Loss by solution in 8 cm of clear rubber tubing.*

In the case of propane the difference between "duplicate" tests is roughtly 20 percent, and there is no reason to believe that differences greater than this may not be expected.

In view of this fact the apparent difference in behavior of carbon dioxide and ethylene shown by one curve of figure 2 from that of ethane and acetylene shown by another curve may well be accidental. In addition, it is somewhat doubtful whether results obtained by the use of relatively long rubber tubing can be applied to the loss of gas under conditions prevailing in method 1. The best conclusion that can be drawn from the data obtained is that the losses of carbon dioxide, ethane, acetylene, and ethylene are all of the same order of magnitude.

(b) LOSSES OF BUTANE WITH GRAY RUBBER TUBING AND WITH LUBRICANTS OF DIFFERENT COMPOSITIONS

In order to establish the magnitude of losses of gas by solution in different lubricants and in gray rubber tubing the data given in figure 3 were obtained. The data obtained with butane in the

unmodified apparatus, figure 1, and with butane in the clear rubber tubing, figure 2, are included for comparison.

The inside dimensions of the glass tube used to obtain the data shown by the curves in figure 3 were approximately the same as those of the rubber tube used for figure 2. The glass was coated on the inside with a thick layer of vaseline or stopcock lubricant, but these layers were not necessarily of the same thickness in the two cases. Very little discussion of these results seems necessary, and it will suffice to say that while gray rubber tubing seems to cause a greater loss than clear rubber tubing, and a greater solubility was indicated in

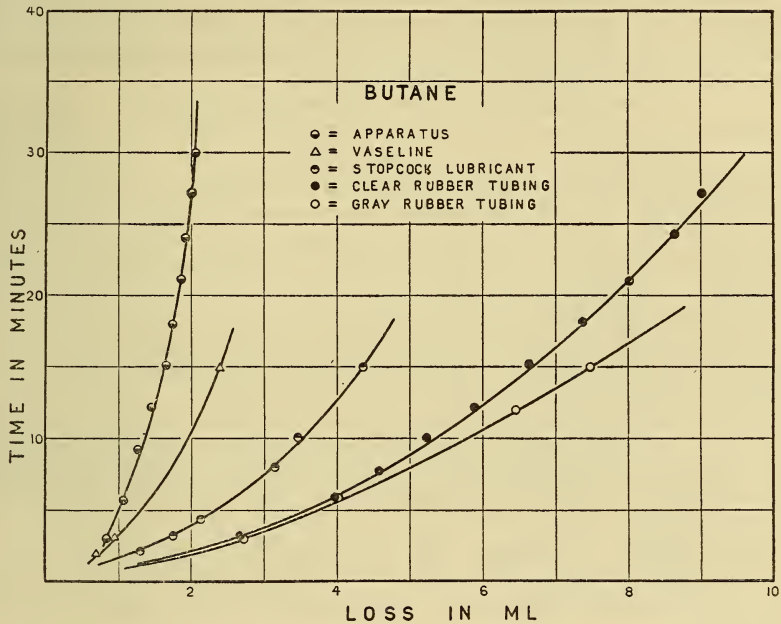

FIGURE 3.—*Loss of butane by solution in rubber tubing and in lubricants.*

the compounded lubricant than in vaseline, the differences have no practical significance as far as an analysis is concerned.

V. APPLICATION TO ANALYTICAL RESULTS

The data indicate that a correction for gas lost by solution in rubber connections and stopcock lubricant is desirable if errors caused by solution are to be avoided in gas analysis.

Since the corrections to be made will vary with each apparatus and the conditions under which it is operated, satisfactory corrections can be deduced only by performing blank analyses in connection with the analyses to which the corrections are to be applied. The blank analysis should be designed so that they will indicate the volume of gas lost by solution and also the volume of dissolved gas that may come out of solution from the connections and lubricant when a different gas is present in the apparatus. This second requirement is particularly important when dealing with the more soluble gases.

It is obvious that the value of blank analyses depend upon how closely they predict what will occur in the analyses to which they are applied. Furthermore, it can be seen that the effect of a variation of time or other condition between the blank and the actual analysis will be more serious when dealing with gases whose rates of solution are rapid.

If the probable error in the measurement of any gas volume is ± 0.02 ml and the probable error in the measurement of the loss of gas by solution (in rubber and lubricant) is ± 20 percent, the following facts obtain:

1. If the measured loss by solution, as shown by blank analyses, is 0.1 ml or less, a correction for the measured loss can be applied with assurance that the analytical results are within experimental error, and represent the best values obtainable.

2. If the measured loss caused by solution exceeds 0.1 ml, the correction for this loss involves an uncertainty which is not within the normal experimental error of the volumetric measurement. This uncertainty becomes larger as the loss by solution becomes larger. Thus, the analyst will become least certain of his results at the very time when the correction to be applied becomes most imperative. Therefore, he can only make the best of a situation which becomes increasingly difficult, knowing that his corrections become more significant as they become less accurate.

In order to illustrate the significance of the loss of gas (by solution) upon the results of an analysis, the following calculations of such analysis are presented:

Case 1.—Assume the sample to be pure carbon monoxide, which is submitted to the analyst as approximately pure carbon monoxide. The analysis is expected to disclose the possible presence of hydrogen or methane (or both) as impurities which are to be determined from *TC*, CO_2 and O_2.

The following conditions will be assumed to prevail: (*a*) that a 50 ml sample of the gas is burned; (*b*) that 0.06 ml of the CO_2 formed is lost by solution, and (*c*) that the gases involved obey the simple gas laws.

Under these conditions the data obtained would be $O_2 = 25.00$ ml, $CO_2 = 49.94$ ml and $TC = 25.06$ ml, and the following results would be reported:

$$CO = \tfrac{1}{3}(4\,CO_2 + TC - 3\,O_2) = 49.94 \text{ ml} = 99.88\%$$
$$H_2 = (TC - O_2) = .06 \text{ ml} = .12\%$$
$$CH_4 = O_2 - \tfrac{1}{3}(CO_2 + TC) = .00 \text{ ml} = .00\%$$

Case 2.—Assume the sample to be pure butane, which is submitted to the analyst to determine the possible presence of propane. Since it is normal practice to calculate the percentages of these two gases from *TC* and CO_2, these factors will be used in the illustrative example. (Such a procedure is not recommended, but is followed here simply because it represents the usual routine.)

The following conditions will be assumed to prevail during analysis: (*a*) that a 10 ml sample of the gas was analyzed. (The size of the sample is limited by the amount of oxygen necessary to burn it. The oxygen must be present in large excess, and must be measured in the burette); (*b*) that 1.0 ml of the sample was lost by solution. (The data given show a loss of 1.8 ml, but other observations show that approximately 0.8 ml of the gas so lost will be regained in 20 minutes

in the presence of a different gas); (*c*) that 0.06 ml of the CO_2 formed is lost by solution; and (*d*) that the gases involved obey the simple gas laws.

Under these conditions, the data obtained would be:

$$S=10 \quad O_2=58.5, \quad CO_2=35.94, \quad \text{and} \quad TC=32.56.$$

This is deduced as follows:

Assuming (*a*) and (*d*)

$$10 \text{ ml } C_4H_{10}+65\text{ml } O_2 \rightarrow 40 \text{ ml } CO_2+35 \text{ ml } TC.$$

Then assuming (*b*)

$$9 \text{ ml (read as 10) } C_4H_{10}+58.5 \text{ ml } O_2 \rightarrow 36 \text{ ml } CO_2+32.5 \text{ ml } TC.$$

And assuming (*c*)

$$9\text{ml (read as 10) } C_4H_{10}+58.5 \text{ ml } O_2 \rightarrow 35.94 \text{ ml } CO_2+32.56 \text{ ml } TC.$$

By the formula commonly used in computing results,

$$C_4H_{10}=2\ (CO_2-TC)=6.76 \text{ ml}=67.6\%, \text{ and}$$

$$C_3H_8=\frac{8TC-7CO_2}{3}=2.97 \text{ ml}=29.7\%$$

In the two examples given above, that of the combustion of carbon monoxide illustrates the minimum error that may be expected in the results when the products of combustion are rich in carbon dioxide. Case 2 which involves the loss by solution of a very soluble gas, butane, in addition to the subsequent loss of a relatively small amount of carbon dioxide illustrates the maximum error that will occur in dealing with gases covered by the data in this paper.

In order to complete the picture it will now be assumed that the analyst had performed blank analyses in addition to the actual analyses cited. It will further be assumed that the error in the blank analysis was 20 percent so that the loss by solution assumed was $.80\times.06=.05$ ml CO_2 and $.80\times1.0=0.8$ ml of butane.

Applying this correction, for loss by solution, to the data from the combustion of carbon monoxide the corrected data become:

$$S=50 \text{ ml}, \ O_2=25 \text{ ml}, \ CO_2=49.99 \text{ ml}, \text{ and } TC=25.01 \text{ ml}.$$

$$CO=\tfrac{1}{3}\ (4\ CO_2+TC-3\ O_2) \ =49.99 \text{ ml} \ =99.98\%$$

$$H_2=(TC-O_2) \ = 0.01 \text{ ml} \ = \ 0.02\%$$

$$CH_4=O_2-\tfrac{1}{3}\ (CO_2+TC) \ = 0.00 \text{ ml} \ = \ .00\%$$

Applying the two "corrections" for loss by solution to the data obtained from the combustion of butane, the "corrected" data become:

$$S \text{ (burned)}=10.0 \text{ ml}-0.8 \text{ ml} \ = \ 9.2 \text{ ml}.$$

$$CO_2=39.94 \text{ ml}+0.05 \text{ ml} \ =35.99 \text{ ml}.$$

$$TC=32.56 \text{ ml}-0.05 \text{ ml}-0.8 \text{ ml} \ =31.71 \text{ ml}$$

$$O_2=58.5 \text{ ml}.$$

Substituting these values in the formulas,

$$C_4H_{10} \ =2\ (CO_2-TC) \ =8.56 \text{ ml} \ =93.04\%.$$

$$C_3H_8 \ =\frac{8TC-7CO_2}{3} \ =0.58 \text{ ml} \ = \ 6.30\%.$$

CONCLUSION

It is customary for the gas analyst to perform two or more analyses with each gas sample in order to confirm the validity of the reported data. The analytical manipulations of these "check" analyses are naturally nearly identical. If the data obtained from the second analysis agrees with the first, the conclusion is that the data are as good as may be obtained under the conditions of the analyses and

the limitations of the apparatus. These limitations or inherent errors, such as loss of gas by solution, are particularly insiduous because they may occur to the same extent in several check analyses and therefore remain hidden. Under such conditions the analyst may be misled regarding the accuracy of the analytical data, and draw erroneous conclusions concerning the composition of the samples.

Losses of hydrocarbons and carbon dioxide and, in some cases, contamination of a fresh sample with residues of gases previously analyzed, may be expected to result from the solubility of hydrocarbons and carbon dioxide in rubber tubing and stopcock grease. In some cases the error introduced may be very large, in other cases it is near the limit of observation. The analyst should have the possibility of such errors in mind at all times and should take such precautions as may be necessary to obtain results within the limit of accuracy needed for the purpose for which the analysis is made. In some cases, the necessary accuracy may be secured by making determinations of and correcting for the loss of gas which takes place in the apparatus.

WASHINGTON, January 13, 1934.