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GASOMETRIC METHOD AND APPARATUS FOR THE ANALYSIS OF MIXTURES OF ETHYLENE OXIDE AND CARBON DIOXIDE

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ABSTRACT

A gasometric method for the analysis of ethylene oxide mixed with carbon dioxide is reported. Ethylene oxide is swiftly and quantitatively removed from the gas phase by a relatively small amount of sulfuric acid. This reagent absorbs over 5,000 times its own volume of ethylene oxide, and the quantity used (only 0.2 ml) dissolves no significant amount of carbon dioxide. The carbon dioxide is absorbed in a concentrated solution of potassium hydroxide. A reproducibility of ±0.05 percent is attained; the accuracy is commensurate. All gases are measured dry in a new apparatus designed to perform this type of analysis rapidly.

CONTENTS

I. INTRODUCTION

The use of ethylene oxide as a fumigant has increased considerably in this country and abroad during the last 8 years. This substance is generally used with about 90 percent of carbon dioxide to produce a noninflammable mixture. The analysis of this simple mixture has caused some difficulty, in spite of the remarkable chemical reactivity of the ethylene oxide. The methods so far reported have been limited in number and are not satisfactorily accurate. They have involved a combination of gravimetric or gasometric methods, always with a final estimation of the ethylene oxide alone by titrimetric procedure. The method here developed involves only direct gasometric measurements made with a standard burette-manometer-compensator unit. Its accuracy is commensurate with that obtained by the best of the former methods, and both components of the mixture may be determined in less time and with less effort than were required previously for the determinations of ethylene oxide alone.

II. PREVIOUS INVESTIGATIONS

Deckert[1] employed the reaction of ethylene oxide with hydrochloric acid and sodium chloride to form glycol chlorohydrin, titrating the excess acid with sodium hydroxide to determine ethylene oxide. Later, Deckert[2] reported a colorimetric method based upon the reaction of ethylene oxide with a concentrated solution of sodium chloride to form glycol chlorohydrin, phenolphthalein and bromothymol blue serving as indicators. He reported a third method (colorimetric)[3] for the examination of air containing traces of ethylene oxide, based on the reaction with potassium thiocyanate, with phenolphthalein as indicator.

According to Lubatti,[4] Deckert's titrimetric method indicated only 90 percent of the ethylene oxide present. Lubatti employed a nearly saturated acid solution of magnesium chloride as an analytical reagent for the examination of samples of liquid ethylene oxide, titrating with sodium hydroxide. The reaction was over 99 percent complete.

More recently the apparatus described by Page[5] was utilized by Lubatti,[6] who modified his original modification of Deckert's method to the extent of adding sodium, lithium, and magnesium chlorides to 0.1 *N* hydrochloric and sulfuric acids, titrating the excess acids with sodium hydroxide.

III. DEVELOPMENT OF A GASOMETRIC METHOD

1. PRELIMINARY CONSIDERATIONS

The reduction in gas volume which occurs when ethylene oxide reacts with reagents of these types was suggested by Deckert[7] as an obvious means of determining ethylene oxide. The gasometric procedure has been employed in several laboratories, but the results have not encouraged publication. The reagents used to absorb ethylene oxide have been aqueous solutions of various salts or mixtures of these prepared indiscriminately. It is not unlikely that these reagents reacted quantitatively with ethylene oxide, since water alone will do so, and with great rapidity if the gas is bubbled through it.[8] The major mistake apparent in these efforts has been the use

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[1] W. Deckert, Z. anal. Chem. **82**, 297–307 (1930).
[2] W. Deckert, Z. angew. Chem. **45**, 559–62 (1932).
[3] W. Deckert, Z. angew. Chem. **45**, 758 (1932).
[4] O. F. Lubatti, J. Soc. Chem. Ind. **51**, 361 (1932).
[5] A. B. P. Page, J. Soc. Chem. Ind. **54**, 421 (1935).
[6] O. F. Lubatti, J. Soc. Chem. Ind. **54**, 424 (1935).
[7] See footnote 1.
[8] Several experimenters state that the reaction is slow. This is not true if an efficient absorbing pipette is employed.

of 100- to 200-ml portions of aqueous reagents in ordinary forms of absorption pipettes. Thus speed of reaction has been attained, but with a grievous sacrifice of accuracy, since carbon dioxide dissolves abundantly in such aqueous solutions. Elaborate precautions have been taken to saturate the reagent (at controlled temperature) with carbon dioxide. This prerequisite to actual analysis not only requires much time, but unfortunately does not accomplish its objective since the dissolved carbon dioxide wanders in two directions: Into the air through the atmospheric arm of the pipette, and into the gas sample during the absorption of ethylene oxide. The amount lost by the reagent to the gas sample may be tediously replaced by repeated passage into the pipette, but the amount lost to the air must be replaced by an equal amount from the gas sample itself, thus causing a proportionately high estimation of ethylene oxide.

A brief outline of a successful gasometric method for the analysis of a mixture of ethylene oxide and carbon dioxide should serve to make this problem clear.

To begin with, the sample taken for analysis must be measured in a dry burette. If the moist burette generally used were employed, water present would react with the ethylene oxide (hereinafter designated C_2H_4O) and alter the composition of the sample before its analysis.

Next, the dry sample must be transferred to a reagent which will quantitatively remove C_2H_4O, without removing CO_2.

Since the reagent which removes C_2H_4O will also add H_2O vapor to the residual gas, this gas must be returned through a suitable desiccant in order that it may reach the burette in a dry state. The difference between the measured dry sample and dry residue should then represent the C_2H_4O in the sample.

Finally, the CO_2 must be removed, and the residual gas returned (after drying) to the burette for measurement. The contraction observed will then represent the CO_2 in the sample.

Since the sample may consist entirely of C_2H_4O and CO_2, a measured volume of dried air must be added during the initial steps of the analysis. This will act as a transfer or "push" gas, and must be inert with respect to the reagents employed. The difference between its volume and the volume of the residual gas observed at the end of the analysis represents the inert content of the sample.

From this outline, it can be seen that the development of a successful gasometric method for the analysis of this mixture will resolve naturally into three separate problems, as follows:

1. Selection of a reagent which is chemically and physically selective with respect to C_2H_4O in the presence of CO_2 and air.
2. Selection of a desiccant which is chemically and physically passive with respect to CO_2 and air.

Since a satisfactory reagent for CO_2 (in the presence of air) already exists, the final problem becomes:

3. Design of a volumetric apparatus capable of performing the necessary procedures indicated.

These problems will be discussed in their order.

2. REAGENT FOR ETHYLENE OXIDE

A suitable reagent for the determination of C_2H_4O must possess the following qualifications:

1. The reagent must react quantitatively with C_2H_4O, completely removing this substance from the gas phase, or replacing it with a stoichiometrically definite volume not equal to its own.
2. The product or products of reaction must possess negligible vapor pressures (or vapors which can be removed chemically without affecting CO_2 or air).
3. The reaction must produce no gaseous by-product (unless this can be removed).
4. The reagent or products of reaction must not react with, or dissolve, significant amounts of CO_2 or air.
5. Since any reagent likely to be conceived will dissolve CO_2 to some extent, the volume of the reagent actually employed must be very small in order to reduce the attendant error to the order of magnitude of the required volumetric precision.
6. The above qualification at once imposes several additional and severe ones. Since the volume of the reagent must be reduced to 0.2 to 0.3 ml, it can most conveniently be confined over mercury. Therefore, it must not react with mercury to produce significant amounts of gas.
7. A pipette of the type mentioned above is at best an inefficient absorber, presenting little contact between gas and reagent. Accordingly, the rate of reaction between the reagent and C_2H_4O must be very rapid.
8. Finally, because of its small volume, and for the sake of convenience, the reagent should have an extremely large capacity for C_2H_4O, so that its frequent replacement may be avoided.

This list of qualifications would appear to be somewhat appalling to the gas analyst; but actually they were easily realized. The behavior of C_2H_4O with various substances was roughly studied in a preliminary set of experiments. C_2H_4O was observed to react readily with the contents of the reagent bottles at hand on the laboratory shelf, such as HNO_3, HCl, H_3PO_4, H_2SO_4, CrO_3, $H_2Cr_2O_7$, $HgNO_3$, etc., in various dilutions with water. As a matter of fact, since C_2H_4O reacts readily with H_2O alone, it seems likely that few inorganic reagents would prevent the formation of the glycol in the presence of water, although some accelerate the reaction. The apparent tendency of C_2H_4O to react with many such mixtures suggests the possibility of a number of satisfactory reagents.

Only one from this list of reagents was selected for extensive study. The reagent selected was a mixture of equal parts of H_2O and concentrated H_2SO_4. This met every one of the qualifications previously delineated. In the event other reagents develop, it would not seem worth-while to issue additional papers for each in turn.

Apparently, the reaction between the diluted H_2SO_4 and C_2H_4O goes through an intermediate state to form ethylsulfuric acid, which breaks down to H_2SO_4 and the first glycol. This in turn reacts with additional C_2H_4O to produce higher glycols, increasing enormously the capacity of the reagent.

The behavior of this reagent with C_2H_4O is interesting. If the gas is confined over mercury within a glass tube, and the reagent is admit-

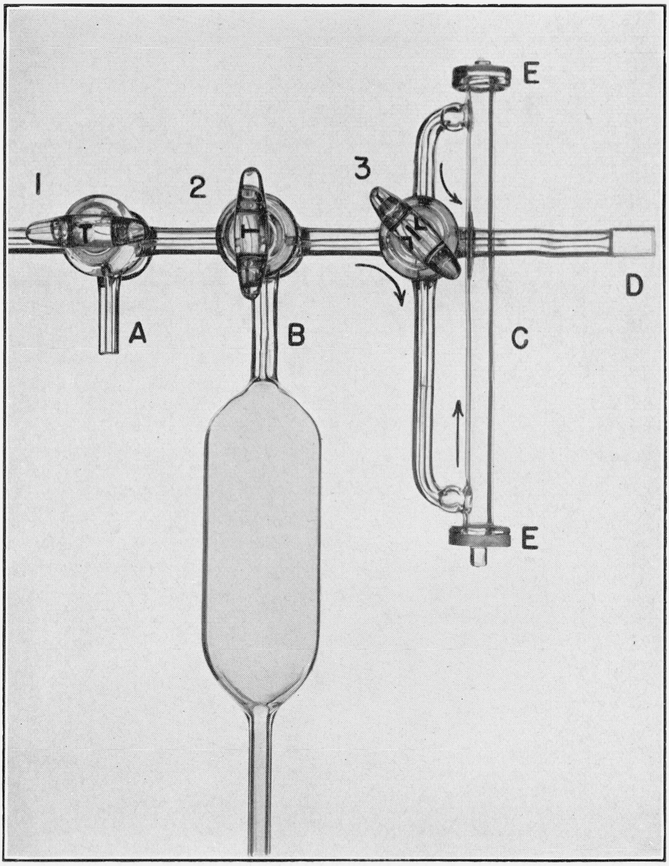

FIGURE 1.—*Reaction unit.*

ted in successive small portions of 0.2 ml each, the initial reaction is very rapid and the final reaction very slow with the addition of each portion of reagent. However, if the wall of the tube is coated with the reagent by shaking, the reaction thereafter is extremely rapid. The glycols which form drain slowly, producing a film or droplets of honey-like consistency over the entire wall of the tube.

Over 2,500 ml of C_2H_4O was passed (at a rate exceeding 200 ml per minute), into a tube containing 0.5 ml of the H_2SO_4 solution. At the end of this experiment, the reaction was still proceeding rapidly and completely. Approximately 2 ml of the glycols had been collected. The capacity of the reagent is accordingly over 1:5000, expressed as a ratio by volume of reagent:C_2H_4O, a novel behavior from the viewpoint of the gas analyst.

There was no direct evidence of the formation of interfering byproducts of the reaction. Acetaldehyde was suspected, but only traces of it were found.

3. SUITABLE DESICCANTS

To qualify for occupancy of the drying tube within the analytical apparatus, a desiccant must possess the following characteristics:

1. It must leave somewhat less water vapor in the dried gas than corresponds to the volumetric accuracy of the apparatus. This limit with respect to the desiccant can be set at 0.02 ml.
2. It should dry the gas rapidly, preferably at the rate of 100 ml per 30 seconds or less.
3. It must not react with CO_2 or air, nor adsorb significant quantities of these gases.
4. It should not react objectionably with C_2H_4O in the event that this gas is accidently brought into contact with it through a mistake in operation.
5. It should be convenient to use.

Of the available desiccants initially suggesting themselves, P_2O_5, $Mg(ClO_4)_2$, $CaSO_4$, and $CaCl_2$ (fused, granular, anhydrous) seemed best suited. These were studied experimentally, and the following facts were ascertained:

1. All four met the first qualification, $CaCl_2$ in its best available form just passing.
2. All four met the second qualification.
3. P_2O_5, $Mg(ClO_4)_2$ and $CaCl_2$ met the third qualification. ($CaCl_2$ must, of course, be of reagent quality. Traces of alkaline impurities must be neutralized by treatment with CO_2+air before the gas analysis.) $CaSO_4$ adsorbed large amounts of CO_2 and was therefore discarded.
4. Of the remaining three desiccants, $CaCl_2$ alone met the fourth qualification completely. This is a "should" and not a "must" qualification, however, since C_2H_4O would not come into contact with the desiccant except by mistake.

If C_2H_4O is inadvertently passed over P_2O_5, the reaction is marked, as is the P_2O_5 with a visible deposit of carbon, which leaves no doubt as to the necessity of its replacement.

$Mg(ClO_4)_2$ is open to a curious objection. A double mistake might conceivably result in (a) bringing H_2SO_4 into contact with this desiccant, and later (b) bringing C_2H_4O into the same tube. It is not

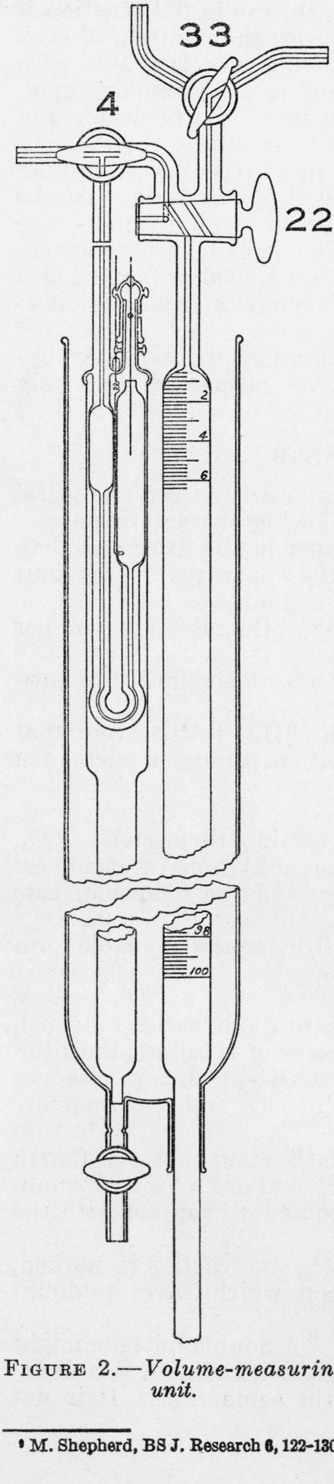

FIGURE 2.—*Volume-measuring unit.*

probable that such mistakes would be made; but if they were, a serious explosion might occur. $Mg(ClO_4)_2$ was actually used in the analytical work which follows. Since it demonstrated no marked superiority, it had probably best be laid aside in this instance.

5. Of the two remaining desiccants, $CaCl_2$ is by far more convenient to use. However, P_2O_5 may, without too great difficulty, be sifted onto glass wool within the drying tube of the apparatus. This is best done by plugging a tube (smaller than the drying tube) at one end with glass wool, drawing (by vacuum) P_2O_5 from the reagent bottle into this tube, and finally inserting the small tube into the desiccating tube of the apparatus, discharging its contents therein by means of a thin glass rod. Once this tube is filled, prolonged service is to be expected.

The analyst will probably make his own choice between P_2O_5 and $CaCl_2$. With respect to H_2O and CO_2, P_2O_5 offers the best chemical behavior. Both desiccants gave good analytical results. In any event, the same desiccant should be used in both drying tubes attached to the apparatus.

4. DESIGN OF THE VOLUMETRIC APPARATUS

In measuring the mixture of $C_2H_4O+CO_2$ gasometrically, it is obvious that the burette must be dry. The dry burette accordingly should be complemented with a dry compensator. The burette and compensator-manometer unit of our standard gas-analysis apparatus [9] served satisfactorily.

Aside from measurement, it is necessary only to transfer the measured dry sample to the reagent which removes C_2H_4O and subsequently remove the water vapor which this reagent adds to the residual gas prior to returning it to the burette. Thereafter, the residue is to be passed into a reagent which removes CO_2, and the residual gas dried and measured.

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[9] M. Shepherd, BS J. Research 6, 122–130 (1931) RP266.

An apparatus[10] by means of which these procedures may be easily achieved is shown in figure 1.

This unit is sealed directly onto the horizontal outlet of stopcock 4 of the burette-manometer-compensator assembly previously mentioned, which is reproduced here for convenience (fig. 2). A thermoplastic cement (pine tar and shellac) serves to make the joint at the sleeve, *D*, (fig. 1). According to tests made, rubber reacted with C_2H_4O too rapidly to permit its use. The cement reacted too slowly to cause significant error. Actually, the main concern is at the sampling inlet.

An ordinary bubbling pipette connected at the outlet, *A*, of T-stopcock 1 is filled with a concentrated solution of KOH to remove the CO_2. (A concentrated solution is used because of the low solubility of atmospheric inerts.)[11]

A reservoir, *B*, connected to T-stopcock 2 serves as the reaction pipette for the C_2H_4O. It is filled with mercury, and a leveling bulb is attached to its lower outlet. The small volume of reagent (0.2 to 0.3 ml of equal parts by volume of H_2O and concentrated H_2SO_4) may be conveniently introduced into *B* by means of a medicine dropper drawn out into a tip which is bent downward at a right angle. This tip may be inserted in the capillary inlet of *B* when the key of cock 2 is removed. One such charge will serve for a hundred or more analyses before it must be removed in the same manner.

The capillary inlet of *B* has a reference or zero mark etched around the stem just under cock 2. The lower outlet of *B* connects to a stopcock by means of nitrometer tubing, around which is placed a compression screw for adjusting the reagent meniscus to this zero mark.

The tube, *C*, contains a desiccant for drying the gases returned from *A* or *B*. Stopcock 3 is drilled with three bores, as indicated on the handle. When turned 45° counterclockwise to the position shown in figure 1, tube *C* is by-passed, and gas *from* the burette flows directly within the horizontal distributor to either *A* or *B*. When the cock is turned in the position shown, gas flowing from *A* or *B to* the burette must pass through *C*, entering at the bottom of this tube and leaving the top, as indicated by the directional arrows.

The tube, *C*, is closed by means of plates, *E–E*, which are ground flat to fit corresponding ground seats at the ends of *C*. A heavy lubricant serves to seal them. They are held in position by two coil springs fastened to saddles of sheet metal, which, in turn, fit over the glass knobs of the end plates, *E–E*. Thus, the tube, *C*, may be easily opened in position on the apparatus for supplying or removing desiccants. Plugs of glass wool at the ends of *C* keep the desiccants in place.

The gas volume of *C*, when filled with desiccant, is small enough so that changes of 0.2° C. in room temperature will produce no significant error in comparing volumes during an analysis. The time required for an analysis is so short that trouble from changing temperature should never occur.[12]

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[10] This apparatus was designed by Shepherd. The unit comprising cock 3 and tube *C* is to be used in a multiple assembly in a new type of gas-analysis apparatus now under test.

[11] J. R. Branham and M. Sucher, J. Research NBS **21**, 63 (1938) RP1113.

[12] One of the most embarrassing questions asked the authors with respect to any type of analysis is, "How long does it take to do it?" There are so many factors involved—the accuracy desired, the composition of the mixture, and, of course, the analyst—that definite answers cannot be given. But in the present instance, it may be of interest to know that it is possible to complete an analysis in 15 minutes, operating carefully.

To complete the apparatus, a drying tube is connected to the left-hand outlet of stopcock 33 of the burette (fig. 2), and the source of sample to the right-hand outlet of the same cock. These connections were made with sleeve joints and thermoplastic cement in the present work, but ground joints would be preferable.

The apparatus described in figure 1, as previously noted, may be used in conjunction with the regular volumetric unit and with the supporting frame of our standard gas analysis apparatus. If, however, the number of samples to be analyzed would justify a separate apparatus for the purpose, the following modifications would improve the unit somewhat:

1. The burette should be blown with a 20-ml bulb at the top, with intervals on the stem from approximately 20 to 100 ml. This would (a) shorten the apparatus or (b) permit estimations of intervals of smaller volume if the apparatus were not shortened.
2. The two outlets of stopcock 33 of the burette (fig. 2) should terminate in interchangeable ground-glass joints (male members), to permit easy connection to an auxiliary drying tube and source of sample.
3. The sleeve, *D*, (fig. 1), should be tapered (female) to fit a corresponding taper (male) on the outlet of cock 4 (fig. 2).

5. VOLUMETRIC BEHAVIOR OF THE DRY APPARATUS

Before developing the analytical procedure, the volumetric behavior of the dry burette and compensator was studied experimentally. The following facts were ascertained:

1. With a desiccant in the tube, *C*, and with the reservoir, *B*, the burette and the compensator dried, a volume of dried air could be repeatedly measured, transferred from the burette to the reservoir and back, and even allowed to stand overnight, with no significant change in volume (±0.02 ml). Indeed, there are indications that the dry system might prove more accurate than the saturated (wet) system ordinarily employed.
2. With water in the reservoir, *B*, dry air transferred to *B* and returned to the burette through *C* (containing any desiccant later employed) gained approximately 0.05 to 0.08 ml if the rate of return exceeded 70 ml per 20 seconds. However, no change of volume was noted at the lesser rates of gas flow employed. Returning a gas from *B* through *C* in 30 seconds insures drying.
3. If dried air is passed directly over water in *B* and returned to the burette, by-passing *C*, the volume is increased to correspond to the existing vapor pressure of water. Thereafter, if the moist air is passed back and forth between *B* and the burette through the desiccant, the volume gradually returns to its original dry value. Approximately 4 or 5 passages (2 minutes each) through the desiccant are required to restore the dry condition, since adsorbed water is apparently given up reluctantly by the burette wall. This illustrates the importance of always returning gas to the burette through the tube, *C*.

6. ANALYTICAL PROCEDURE

The following detailed procedure was developed during the course of a few preliminary analyses, and of the analyses reported in table 1.

Initial drying of apparatus.—The compensator was dried by alternate evacuation and filling with air dried over P_2O_5. (A small amount of desiccant left permanently in the bottom of the compensator would probably be desirable in an apparatus to be used for this type of analysis only.) The burette was dried by repeatedly passing air in and out through the desiccant connected to cock 33 (fig. 2). The distributor was dried by passing air through *C* to *A* and back. About 10 passages of 2 minutes each are required for drying, if no water was originally visible. Once dry, the apparatus should remain so.

Analytical technique.—The distributor, manometer, and *C* are filled with dried air and adjusted to the fixed pressure of the compensator.

Approximately 60 ml of the $C_2H_4O+CO_2$ mixture to be analyzed is drawn into the burette. With cock 22 closed the pressure is balanced against atmospheric with the leveling bulb, so that a minimum amount of gas will later flow between the burette and manometer. Cock 4 (fig. 2) is then turned to the position ⊢ to connect the manometer with the burette; the pressure is balanced against the compensator, cock 4 is turned to the position ✓ to disconnect the burette from the manometer and train, and the volume of the sample is read. Cock 3 (fig. 1) is turned to the position $\overset{\vee}{\underset{\wedge}{-}}$, the leveling bulb attached to *B* is lowered slightly to reduce the pressure therein, cock 2 to the position ⊢, and cock 4 to the position ⊥. The sample is transferred to *B*, the leveling bulb being dropped to maintain approximately atmospheric pressure in *B*. When the mercury in the burette reaches cock 22, it is turned to connect to cock 33 and the line between them is flushed with mercury. Cock 33 is then turned to connect the burette to the source of dried air, 25 to 30 ml of which is taken into the burette and measured exactly as was the sample. The gas in the arm of the manometer connecting to the distributor is then displaced to the burette, cock 4 is turned to the position ✓, the pressure of the gas in the burette adjusted to slightly in excess of atmospheric by the leveling bulb, and the air is then transferred to *B* with cock 4 in the position ⊥. The dry air has now swept the $C_2H_4O+CO_2$ into *B*, where the mixture is allowed to stand 1 minute. Agitation by means of mercury flow is not necessary after the first passage of the first analysis. Cock 3 is now turned to the position ┐╲└ and the residual gas (minus C_2H_4O) is returned through *C* to the burette, 30 seconds being taken for passage through *C*. The volume is measured as before, the contraction noted being computed as C_2H_4O.

The gas in the distributor arm of the manometer is again displaced to the burette, and thence transferred to the pipette, *A*, containing a solution of KOH, being routed through *C*, both back and forth. During the eighth and tenth passages *into A*, cock 3 is turned for a second to the position $\overset{\vee}{\underset{\wedge}{-}}$ to displace CO_2 trapped in the straight bore of this cock. At *no time* must gas by-pass *C* on the way *back* to the burette. After the tenth passage, the residual gas (minus CO_2) is measured and the contraction computed as CO_2. (Ten passages are used to insure complete removal of CO_2 from the tube, *E*, and the distributor, by dilution.) The difference in volume between this residue and the dry air originally taken for a transfer gas is computed as the inert content of the sample.

IV. ANALYSES OF MIXTURES OF ETHYLENE OXIDE AND CARBON DIOXIDE

1. PREPARATION OF MIXTURES FOR ANALYSIS

To test the method, apparatus, and procedure just discussed, two mixtures of C_2H_4O and CO_2 were prepared and analyzed. Both of these mixtures were made to contain approximately 10 percent of C_2H_4O by volume, which corresponds to the mixture used for fumigating. The mixtures were prepared in a 5-liter glass flask to which a barometric manometer was attached. The flask was evacuated, C_2H_4O was admitted until the manometer registered a pressure of approximately 75 mm, and CO_2 was then admitted until the pressure reached approximately 750 mm. The room temperature was observed to remain constant (±0.1° C). The two gases, of almost identical molecular weights, were allowed to mix for several days.

Convection was occasionally induced by local warming of the flask. The flask was then joined to the burette as previously described, and samples were withdrawn using the mercury within the burette as a pump.

The composition of the samples prepared in this manner was not necessarily expected to check the composition as determined by the analysis, even assuming absence of significant errors in both cases. Since the pressure-volume relationships existing during the preparation and during the analysis of these mixtures are different, the deviations of the gases and their mixtures from the behavior prescribed for ideal gases could account for differences in the composition as measured in the two cases.

2. PURITY OF THE ETHYLENE OXIDE

The C_2H_4O used in preparing the two mixtures was purified in a large commercial rectifying column. Approximately 10 liters of this was stored as a liquid in a cylinder. About one-third of the contents of this cylinder had been withdrawn before the present use of the gas.

The completeness of reaction between this C_2H_4O and the H_2O-H_2SO_4 reagent employed during the analyses was determined as follows:

1. 30.08 ml of dried air was measured in the burette and transferred to the reservoir, *B*, containing the reagent.
2. 274 ml of C_2H_4O was measured in three portions and transferred to *B*. (The reaction was so rapid that only with great difficulty could the mercury in *B* be prevented from being drawn into the horizontal distributor.)
3. The residual volume was passed through $CaCl_2$ in *C*, and measured in the burette as 30.53 ml.
4. The difference between the initial and final volumes corresponds to 0.017 ml of "inert" per 10 ml of C_2H_4O. Since 6 ml of C_2H_4O is the amount in the average sample, approximately 0.01 ml of the C_2H_4O used did not react or was inert during each analysis. This is less than the expected volumetric error.

The above test does not preclude the possibility that a compound other than C_2H_4O was present and reacted with the solution of H_2SO_4. The purification of the C_2H_4O by rectification makes such a possibility remote; and analyses of $C_2H_4O+CO_2$ mixtures obtained from the same source as that supplying the present C_2H_4O, made by isothermal fractional distillation in our laboratory, failed to disclose a notable impurity in the C_2H_4O fraction.

3. PURITY OF THE CARBON DIOXIDE

The carbon dioxide used was drawn from the last half of a cylinder of liquid obtained from a commercial source. Its "purity," so far as this work is concerned, was tested as follows:

1. Four volumes totalling 384 ml of CO_2 were measured; 30.43 ml of air was measured separately.
2. These gases were transferred to the pipette containing a saturated solution of KOH, first without bubbling, and finally with repeated bubbling passages.
3. The residual air was dried in *C* and measured as 30.54 ml. This corresponds to 0.03 ml of "inert" per 100 ml of CO_2, or about 0.016 ml per analysis. (A small amount of this inert may have been

air displaced from the solution of KOH during the absorption of CO_2.) This is of the same order of magnitude as the volumetric accuracy at its best.

4. ANALYSIS OF MIXTURE 1

According to the pressures observed in preparing this mixture, its composition was calculated to be:

	(%, by volume; or mole %, assuming ideality)
C_2H_4O	9.59 ±0.03
CO_2	90.15 ±.03
Air	0.26 ±.03

Correcting these for the amount of inert found in the C_2H_4O and CO_2:

C_2H_4O	9.57 ±0.03
CO_2	90.12 ±.03
Inert	0.31 ±.03

TABLE 1.—*Analyses of mixture 1*

Amount of reagent	Desiccant	Analysis number	Percentage, by volume Δ=deviation from average					
			C_2H_4O	Δ	CO_2	Δ	Inert	Δ
ml 2.0	$Mg(ClO_4)_2$	1	9.91	0.05	89.91	0.12	0.19	0.07
		2	9.81	.05	89.98	.05	.22	.10
		3	9.84	.02	90.14	.11	.02	.10
		4	9.87	.01	90.07	.04	.06	.06
Average			9.86	±0.03	90.03	±0.08	0.12	±0.08
0.3	$Mg(ClO_4)_2$	5	9.66	0.04	90.08	0.08	0.27	0.04
		6	9.58	.04	90.12	.04	.30	.07
		7	9.63	.01	90.16	.00	.22	.01
		8	9.61	.01	90.27	.11	.12	.11
Average			9.62	±0.03	90.16	±0.06	0.23	±0.06
0.3	$CaCl_2$	9	9.55	0.04	90.17	0.02	0.28	0.02
		10	9.57	.02	90.20	.05	.24	.02
		11	9.60	.01	90.09	.06	.32	.06
		12	9.64	.05	90.15	.00	.20	.06
Average			9.59	±0.03	90.15	±0.03	0.26	±0.04
0.3	P_2O_5	13	9.73	0.06	89.99	0.17	0.28	0.11
		14	9.75	.08	90.15	.01	.09	.08
		15	9.64	.03	90.11	.05	.24	.07
		16	9.56	.11	90.39	.23	.05	.12
Average			9.67	±0.07	90.16	±0.12	0.17	±0.10
Average 5 to 16, incl			9.63	±0.05	90.16	±0.07	0.22	±0.07
0.3	$CaSO_4$	17	17.3	(a)	(a)	(a)	(a)	(a)
		18	16.6					
		19	17.7					

[a] Not determined.

The analyses of this mixture are given in table 1. Determinations 5 to 16, inclusive, made with 0.3 ml of reagent and with three different desiccants, give the following average composition:

	(%, by volume, as observed)
C_2H_4O	9.63 ±0.05
CO_2	90.16 ±.07
Inert	0.22 ±.07

This agreement is closer than was to be expected.

A study of the data noted in table 1 discloses the following facts:

1. The value for C_2H_4O is apparently 0.2 percent too high, and that

for CO_2 correspondingly too low, if 2 ml of the H_2SO_4 reagent is used instead of 0.3 ml. (Compare the average of determinations 1 to 4 with the average of 5 to 8.) This illustrates the effect of the solubility of CO_2 in the aqueous reagent, and the importance of reducing the volume of the reagent to a working minimum.

2. The results obtained when the desiccants Mg $(ClO_4)_2$, $CaCl_2$ and P_2O_5 are used are concordant, since no significant differences occur between the averages for the determinations 5 to 8, 9 to 12, and 13 to 16, inclusive. When $CaSO_4$ is employed, the results are aberrant. (Note determinations 17 to 19.)

3. The reproducibility attained is adequate.

5. ANALYSIS OF MIXTURE 2

The analysis of this mixture was a slightly more extended effort than that of the first one. According to the pressures observed when preparing the mixture, the composition (corrected for inert found in C_2H_4O and CO_2) was as follows:

	%, by volume
C_2H_4O	9.97 ±0.03
CO_2	89.98 ± .03
Inert	0.05 ± .03

The average of 28 determinations reported in table 2 shows the composition of this mixture to have been:

	%, by volume
C_2H_4O	9.93 ±0.04
CO_2	90.02 ± .05
Inert	0.05 ± .04

TABLE 2.—*Analuses of mixture 2*

Desiccant	Analysis number	Percentage, by volume Δ=deviation from average						
		C_2H_4O	Δ	CO_2	Δ	Inert	Δ	Total
$CaCl_2$	1	9.96	0.03	89.84	0.15	0.20	0.12	100.00
	2	9.86	.07	90.01	.02	.12	.04	99.99
	3	9.82	.11	90.08	.09	.09	.01	99.99
	4	9.93	.00	89.99	.00	.08	.00	100.00
	5	10.08	.15	89.92	.07	.00	.08	100.00
	6	9.91	.02	90.07	.08	.02	.06	99.99
	7	9.83	.10	90.02	.03	.15	.07	100.00
	8	9.98	.05	89.99	.00	.04	.04	100.01
	9	9.98	.05	89.88	.11	.13	.05	99.99
	10	9.91	.02	90.02	.03	.07	.01	100.00
	11	9.93	.00	90.05	.06	.02	.06	100.00
	12	9.95	.02	90.00	.01	.05	.03	100.00
Average	--------	9.93	±0.05	89.99	±0.05	0.08	±0.05	-------
$CaCl_2+P_2O_5$	13	9.93	0.01	90.01	0.04	0.06	0.03	100.00
	14	9.99	.07	89.95	.10	.06	.03	100.00
	15	9.90	.02	90.06	.01	.04	.01	100.00
	16	9.92	.00	90.05	.00	.03	.00	100.00
	17	9.85	.07	90.15	.10	.00	.03	100.00
	18	9.95	.03	90.05	.00	.00	.03	100.00
Average	--------	9.92	±0.03	90.05	±0.04	0.03	±0.02	-------

TABLE 2.—*Analyses of mixture 2*—Continued

Desiccant	Analysis number	Percentage, by volume Δ=deviation from average						
		C_2H_4O	Δ	CO_2	Δ	Inert	Δ	Total
P_2O_5	19	10.01	0.07	89.99	0.06	0.00	0.02	100.00
	20	9.99	.05	90.01	.04	.00	.02	100.00
	21	9.93	.01	90.05	.00	.02	.00	100.00
	22	9.97	.03	90.03	.01	.00	.02	100.00
	23	9.96	.02	90.04	.01	.00	.02	100.00
	24	9.91	.03	90.07	.02	.02	.00	100.00
	25	9.83	.11	90.17	.12	.00	.02	100.00
	26	9.90	.04	90.10	.05	.00	.02	100.00
	27	9.93	.01	90.03	.02	.04	.02	100.00
	28	9.95	.01	89.97	.08	.08	.06	100.00
Average	--------	9.94	±0.04	90.05	±0.04	0.02	±0.02	--------
Average of all analyses	--------	9.93	±0.04	90.02	±0.05	0.05	±0.04	--------

The agreement in this case is about as close as before.

For the convenience of study, the data in table 2 include the deviation of each analysis from the average, the average and the average deviation of each of the three groups of analyses, and the total averages and deviations for the entire series. A study of these data gives the following information:

1. So far as the C_2H_4O is concerned, P_2O_5, $CaCl_2$, and a mixture of the two serving as the desiccant are equally good.

2. The CO_2 tends to be slightly lower when $CaCl_2$ alone is employed. However, the difference between the amount obtained when using this desiccant, and the amounts obtained when using P_2O_5 or $P_2O_5+CaCl_2$ is a matter of no concern.

3. The results on the whole are concordant, and the reproducibility attained should satisfy the general need (±0.05 percent). The maximum deviation noted was 0.15 percent, which should serve to indicate the desirability of check determinations.

It may be noted that the remarkable totals obtained (last column) have little significance other than to testify to the fact that no measurable amount of air leaked out of the apparatus during the analysis.

V. ACCURACY OF THE METHOD

1. PRESSURE-VOLUME CONSIDERATIONS

So far we have made mention of reproducibility only. This is as far as the gas analyst has usually found it convenient to go. Reproducibility, often under the pseudonym of precision, has long masqueraded under the cloak of accuracy. It is a demonstrable entity, and can be captured by anyone with sufficient patience. Accuracy is not so easily demonstrated. This is unfortunately true in the present instance.

If two gases of known and satisfactory purity, which deviate by no significant amount from the formulas laid down for ideal gases either separately or mixed, had been mixed according to the pressure method employed in preparing the samples previously analyzed, then, indeed, a definite figure for the accuracy of this method could be expressed.

But these two gases, C_2H_4O and CO_2, are known to deviate from ideality as separate gases, and the extent of the deviation of C_2H_4O has not been measured. Worse yet, their behavior when together, and when mixed with air, has not been reported. It seems unreasonable to suppose that these two, noticeably imperfect with respect to Boyle's law *as individuals*, would strictly observe only *one* of the perfect gas laws when brought together. Thus it seems scarcely consistent to assume deviations from Boyle's law and ignore deviations from the unnamed laws of additive volumes—an assumption that has already served as the thesis in the development of some impressive formulas for correcting gasometric analyses.[13]

It will be worth while to show experimentally the behavior of these two gases when mixed, in order to illustrate the danger of making the above assumption.

C_2H_4O will vary from Boyle's law considerably more than will CO_2. For this reason, the samples were prepared by measuring C_2H_4O at a low pressure, in which state it could be expected to more nearly behave itself. Even so, it would not be safe to compute the gravimetric composition of this mixture from such pressure data. Reflection over the following data will serve to support this feeling in the matter.

Suppose 40 ml of dry air is measured in the burette of the apparatus used for these analyses. If it is then stored, and 40 ml of dry CO_2 is measured at the same temperature and pressure—and if, now, the 40 ml of air is returned to mix with the 40 ml of CO_2, what would the volume be? This experiment was performed, and the resulting volume (average of 10 determinations) was 80.06 (± 0.02) ml. Next, 40 ml of air and 40 ml of C_2H_4O, measured separately as before, were mixed; the resulting volume (average of 10 determinations) was 80.37 (± 0.04) ml. Now, 40 ml of CO_2 and 40 ml of C_2H_4O were measured separately, and mixed. If a law of ideal mixing prevailed, the expected volume would be 80.00 ml. On the other hand, it might be inferred from the above data that the combined volumes of these two gases would be either 80.43 or 80.21, depending on the particular assumption invoked. But the average of 10 determinations was 80.13 (± 0.01) ml. (40 ml of air+40 ml of air were measured as above to check burette calibration and reproducibility.) It is true these measurements are not sufficiently accurate to justify formulation of equations defining the exact behavior on mixing; but the order of magnitude of the differences is certainly quite significant. The results are convincing enough evidence that the volume relationships on mixing in this gas analysis (and in others) should be investigated. Without such investigation, it is impossible to say whether or not such behavior on the part of gas mixtures will cause significant error.

To get a clearer picture of the pressure-volume relationships existing during this analysis, consider the volumes actually observed. These are (average values):

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[13] Dalton's law, apparently an extension of the law of Henry, has been interpreted in modern textbooks as meaning that the total pressure of a mixture of gases is equal to the sum of the partial pressures of the components. The gases are, therefore, still thought of individually, and one is considered to have no physical effect on the others. This concept has been extended in some texts, and in the minds of many experimenters, to be the practical equivalent of the statement that the total volume of a mixture of gases is equal to the sum of the volumes of the components measured separately, and, of course, at the same temperature and pressure. The latter statement must necessarily involve Boyle's law, and, in the absence of a formal sponsor, it is difficult to name any law of additive volumes. The point so far not taken into account by gas analysts is that mixed gases may not behave as individuals. Thus, if two gases are each measured separately at the same temperature and pressure, the sum of their volumes may not be equal to the total volume of the mixed gases (measured at the same temperature and pressure); and the deviation from this sum may be significantly different from the deviation that might be expected from the law of Boyle alone.

1. The sample is composed of 54 ml of CO_2+6 ml of $C_2H_4O=V_1$.

2. 24 ml of air, measured separately from V_1, and used as an inert transfer gas$=V_2$.

3. 54 ml of CO_2+24 ml of air, the residue after absorption of $C_2H_4O=V_3$.

4. 24 ml of air, the residue after absorption of $CO_2=V_4$.

The analysis is computed:

$$\frac{V_1+V_2-V_3}{V_1}=C_2H_4O;\ \frac{V_3-V_4}{V_1}=CO_2.$$

Of these volumes, V_2 and V_4 are definite; but V_1 and V_3 must be evaluated, since they cannot be arrived at by simple arithmetic.

In order to evaluate V_1 and V_3, the following measurements were made:

1. 54 ml of CO_2 and 6 ml of C_2H_4O were measured separately and when mixed, both gases being dry and at the same condition of temperature and pressure (approx. 1 atm, 25° C). The average of 10 determinations gave this result:

$$54 \text{ ml of } CO_2+6 \text{ ml of } C_2H_4O=60.07\ \pm 0.03 \text{ ml}=V_1, \text{ above.}$$

2. The above measurement was verified by 10 determinations of 54 ml of air+6 ml of air, which served to check the burette calibration and manipulation.

3. 54 ml of CO_2+24 ml of air, measured separately and mixed as before, gave as the average of 10 determinations:

$$54 \text{ ml of } CO_2+24 \text{ ml of air}=78.04\ \pm 0.02 \text{ ml}=V_3, \text{ above.}$$

4. The above measurement was verified by 10 determinations of 54 ml of air+24 ml of air, to check the burette calibration and the manipulation.

5. The measurements made above were further authenticated by passing measured volumes of C_2H_4O and of CO_2 from the burette to the storage reservoir and back, without significant gain or loss of volume.

These evaluations of V_1 and V_3 at once disclose deviations whose order of magnitude (0.1 percent) could produce significant error. But fortunately in this particular instance the computation partially cancels the effect of deviation from ideality. Thus, the deviations, if taken into account, would increase the C_2H_4O by only 0.05 percent and the CO_2 by 0.07 percent.

2. GRAVIMETRIC DETERMINATION OF ACCURACY

While the above measurements give assurance that the accuracy of the method probably is commensurate with the reproducibility obtained, a definite experimental check is in order. The accuracy was, therefore, determined by preparing several mixtures of $C_2H_4O+CO_2$ ranging in composition from about 7 to 12 percent of C_2H_4O. These mixtures were made up as before by measurement of pressure at fixed volume and temperature, but at the same time the composition was determined gravimetrically, and by the analytical method here reported.

(a) APPARATUS

The apparatus employed is shown in figure 3. It comprises a 5-liter flask, *C*, to which is attached a barometric manometer, *B*. A small brass cylinder, *A*, fitted with a needle valve of the vacuum type, connects to *C* through an interchangeable ground joint. An auxiliary flask, *E*, may be attached at the same joint and serves as a sample pipette. The flask and connections may be evacuated by a pump through cock 1, and supplied with C_2H_4O and CO_2 through the two inlets of cock 4.

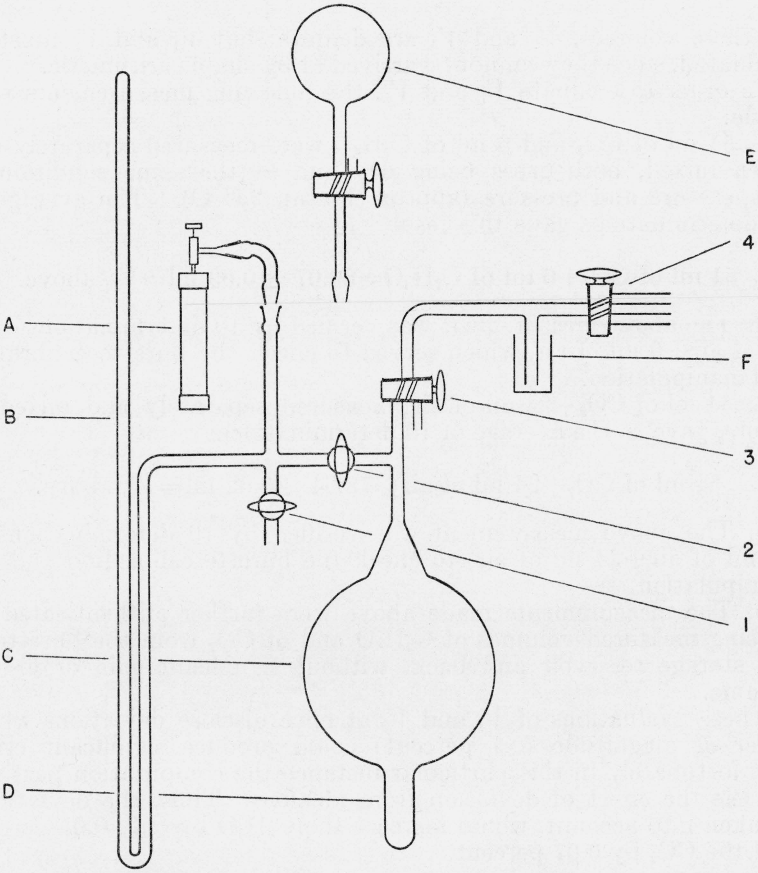

FIGURE 3.—*Apparatus for preparing known mixtures.*

(b) PROCEDURE

The procedure is as follows: Flask, connections, and cylinder *A* are thoroughly dried and evacuated. The manometer is read, *A* and 2 are closed, *A* is removed, weighed, replaced, and the connections evacuated. Cock 1 is then closed and 2 opened. C_2H_4O is allowed to purge through the atmospheric outlet of cock 3 and the safety seal, *F*, immersed in mercury, and then slowly admitted to the flask maintaining excess flow at *F*. Cock 3 is closed when the desired pressure is attained, *A* is immersed in liquid air, its valve opened, and the C_2H_4O condensed therein. The pressure is observed, the valve closed, liquid air placed around the tube, *D*, at the bottom of the flask, and the pressure again observed. C_2H_4O and CO_2 will condense to negligible pressures at −190° C; but very small traces of air in these gases will prevent their complete transfer to *A* within reasonable time, by accumulating at the opening of the needle valve, and offering a plug of uncondensed gas through which the final small portions of C_2H_4O and CO_2 must diffuse slowly. Most of the gas condensed rapidly in *A*, but the final traces were transferred slowly. Rather than wait for the tardy diffusion to occur, a gravimetric correction was made for 0.2- to 4-mm residual pressure. Actually, this introduced the greatest uncertainty in the measurements, and would be avoided in more exacting work. Cock 2 and *A* are both closed, and *A* is removed and weighed. Repeated weighings were made to insure reproducible temperature and humidity conditions, and against leakage of valve.

After weighing cylinder *A* it is replaced, the connections are evacuated, and the C_2H_4O is condensed in *D*. A is closed, and the C_2H_4O is allowed to evaporate in *C*. The pressure and temperature are observed. CO_2 is now purged through 3 and the desired amount is then admitted into *C*. The pressure and temperature are observed. The two pressure observations from which the composition is calculated are thus made within a relatively short interval of time, and temperature conditions remain comparable. The $C_2H_4O+CO_2$ is then condensed into *A* at −190° C. The pressure is observed, *A* is closed, *D* is immersed in liquid air, and the pressure is again observed. Cock 2 is closed, and *A* is removed and weighed.

A is then replaced, the connections are evacuated, and the mixture is condensed in *D*. Cock 2 is closed, the mixture is allowed to evaporate and is stirred by thermal convection, *E* replaces *A*, the connections are evacuated, and a sample taken into *E* from *C* for analysis.

(c) RESULTS

The results of the determinations made with this apparatus and in this manner are given in table 3. Five mixtures were investigated, since some differences might be expected because of the different pressure-volume relationships existing. The mixtures were made up at different temperatures (26° to 30° C), and analyzed at different temperatures (25° to 31° C), so that any probable effect of temperature is accounted for in the data. The range studied covers what may be expected in commercial use.

TABLE 3.—*Comparison of the composition of five mixtures of* $C_2H_4O+CO_2$ *as determined by three methods:*

M=Amount of C_2H_4O, expressed as mole percent calculated from observed gravimetric data:

$$\frac{100\ N_{C_2H_4O}}{\text{Total } N}$$

P=Amount of C_2H_4O calculated from observed pressures:

$$\frac{100\ P_{C_2H_4O}}{\text{Total } P}$$

V=Amount of C_2H_4O, expressed as percent by volume as determined from gasometric analysis:

$$\frac{100\ V_{C_2H_4O}}{\text{Total } V}$$

If the ideal gas laws were obeyed, these three would all be expressions of mole percent, and would agree within the limits of error of the observations, assuming the reaction involved in the data V were quantitative.

Mixture number	Percentage of C_2H_4O			Percentage of C_2H_4O	
	M[a]	P	V	$M-P$	$M-V$
1	7.01	7.06	7.00	−0.04	+0.02
2	8.71	8.78	8.67	−.07	+.04
3	9.92	9.97	9.77	−.05	+.15
4	11.14	11.18	11.07	−.04	+.07
5	12.13	12.13	12.14	0	−.01
Algebraic averages				−0.04	+0.05

[a] Within the significance of the present work, these values may be taken directly as an expression of percentage by weight, since the molecular weights of the two gases are very nearly the same.

The data given show the differences existing between the composition, expressed as percentages of ethylene oxide, as determined (M) gravimetrically according to the method just described, (P) by the measurement of pressure at fixed volume, and (V) by actual gasometric analysis, according to the method described in this paper.

A glance at these data discloses the following facts:

1. The amount of C_2H_4O, as determined by observed pressures, is in general about 0.04 percent higher than that measured gravimetrically.
2. The amount of C_2H_4O as measured by the gasometric analysis, is in general about 0.05 percent lower than that measured gravimetrically.
3. The accuracy attained by the gasometric analytical method, in the range of compositions investigated, is commensurate with the reproducibility of the method. The average deviations observed over the range of composition investigated may be applied as corrections of the gasometric results (if desired) in computing mole percent or percent by weight.

VI. NOTE ON SAMPLING

The fumigant is usually obtained as a mixture of liquid C_2H_4O and CO_2 under pressure in a cylinder. Some cylinders are equipped with a connection leading from the valve to the bottom, so that the contents may be discharged from the liquid rather than the gas phase. Even so, one must not expect to open the cylinder valve slowly and draw off a sample of gas whose composition approaches that of the liquid within the cylinder. The two gases have widely different boiling points, and will separate notably by distillation when vapor is drawn slowly from the cylinder; and vapor will be drawn from the cylinder if the seat of the valve is warm enough to vaporize CO_2. This vapor will push back liquid trying to escape, and so the C_2H_4O will be effectively separated from the mixture.

The tendency of liquified mixtures to separate under such conditions has long been known and has been studied experimentally. An interesting example of such behavior was observed during the gravimetric preparation of the mixtures here reported. After weighing one of these mixtures, the cylinder containing the liquid (at room temperature) was connected to the evacuated flask, the valve was opened, and the mixture allowed to vaporize into the flask. The pressure within the flask built up *immediately* to 10 to 20 mm in excess of the pressure of the CO_2 alone. Thereafter, the pressure increased *very slowly* to equal that originally observed for the mixture of $C_2H_4O+CO_2$.

The only recourse is an extremely rapid discharge of the cylinder (with valve opened wide) into a long pipe of sufficient diameter so that back pressure or cooling does not cause condensation. Samples may be taken from this discharge tube. Better yet, if the cylinder is discharged completely into a large dry evacuated container used for fumigating, samples from this may be treated with more confidence.

It is also necessary to take the sample in dry containers; and rubber tubing should not be used.

WASHINGTON, July 27, 1938.