ethylglyoxime purified by recrystallization from a small amount of water. The material thus recovered was found to melt[1] sharply at 171.°

The residue of nickel salts left by the ether extraction was now thoroughly shaken with dilute ammonium hydroxide. After filtering, the filtrate was acidified with dilute sulfuric acid to a point where any precipitated nickel salt of methylglyoxime redissolved and the solution instead of having a golden yellow color had become colorless. The mixture was now extracted with ether. The methylglyoxime obtained from the ether extract was freed from traces of dimethylglyoxime by redissolving both in water containing a few drops of dilute ammonium hydroxide and adding to this solution a few drops of very dilute nickel chloride. Since the nickel salt of dimethylglyoxime is practically insoluble in so dilute a solution of ammonia, traces of it would thus be precipitated and can be removed by filtration. This procedure was continued until there was sufficient indication that all of the dimethylglyoxime had been removed. The complete removal of dimethylglyoxime is shown by the appearance of the precipitation of the scarlet modification of the nickel salt of methylglyoxime which readily changes over into the more stable yellow modification, and further by the appearance of a yellowish solution due to the solubility of nickel methylglyoxime in ammonia solutions. The solution was again made just acid with dilute sulfuric acid and the methylglyoxime extracted with ether and resublimed. The resublimed dioxime thus recovered melted[1] at 155-156°.

The residue containing the nickel salt of dimethylglyoxime left by the ammonia extraction was thoroughly shaken with 50 cc. of 5% sulfuric acid and an equal volume of ether. The ether layer containing the free dioxime was evaporated and the dioxime recrystallized from water. The substance thus recovered and purified was found to melt[1] at 234-235°

The accompanying diagram graphically outlines the course of the analysis which isolates from a mixture containing minute quantities of the insoluble nickel salts of the dioximes of these α-diketones, the pure dioximes whose melting point identifies each homolog.

THE SEPARATION OF ETHANE AND ETHYLENE BY FRACTIONAL DISTILLATION IN A VACUUM AT LOW TEMPERATURES.[2]

By G. A. Burrell and I. W. Robertson.

Received February 15, 1915.

This paper shows some experiments made by the authors, at the Pittsburgh Experiment Station of the Bureau of Mines, in separating ethane and ethylene by fractional distillation in a vacuum at low temperatures. In previous communications there was shown the separation of gases

---

[1] Cf. Glyoxime, Beilstein, *Organische Chemie*.

[2] Published by permission of the Director of the Bureau of Mines.

whose boiling points are wide apart: (1) the separation of the constituents in natural gas,[1] and (2) the separation of the illuminants in artificial gas.[2] Some of the constituents of the latter were separated in pairs, *i. e.*, ethane, b. p. —93°, and ethylene, b. p. —103°, were separated together, as were propane, b. p. —45°, and propylene, b. p. —51°. They were finally analyzed together by burning them in oxygen. From the carbon dioxide and contraction produced, the percentage of each was calculated.

It was desirable to learn something of the limitations of this method of separating gases; for instance, just how tedious would be the work involved in separating the gases ethane and ethylene, whose boiling points are only 10° apart, when the percentage of each present was large.

Experimental.

Preparation of Ethane.—Ethane was prepared by the electrolysis of a saturated solution of sodium acetate. The carbon dioxide evolved with the ethane was removed with caustic potash. Air or other gases trapped with the ethane were removed by fractional distillation in a vacuum at temperatures ranging from that of liquid air to —120°.

Preparation of Ethylene.—Ethylene was prepared by heating ethyl alcohol and sulfuric acid together at a temperature of 160°. The evolved gases were purified in the same way as the ethane. The purity of the two gases was determined by combustion analysis.

Vapor Pressures of Ethane and Ethylene.—It was first necessary to determine temperatures at which the separation could be effected, *i. e.*, temperatures at which the vapor pressure of ethane is practically nil and that of ethylene high enough so that the latter could be withdrawn from the mixture, finally leaving all of the ethane behind. It was found that ethane has a vapor pressure at 160° of 1 mm. of mercury, while that of ethylene at the same temperature is 4 mm. At —170° the vapor pressure of ethylene was found to be 1 mm., while the manometer did not register any pressure for ethane. These pressures are accurate to 1 mm. at the lower temperature.[3] Temperature readings were made with a pentane thermometer. A wide variation in temperature represented only a small pressure change at the lowest temperatures. The foregoing vapor pressures showed that the separation could probably be accomplished at temperatures of —170° or slightly higher.

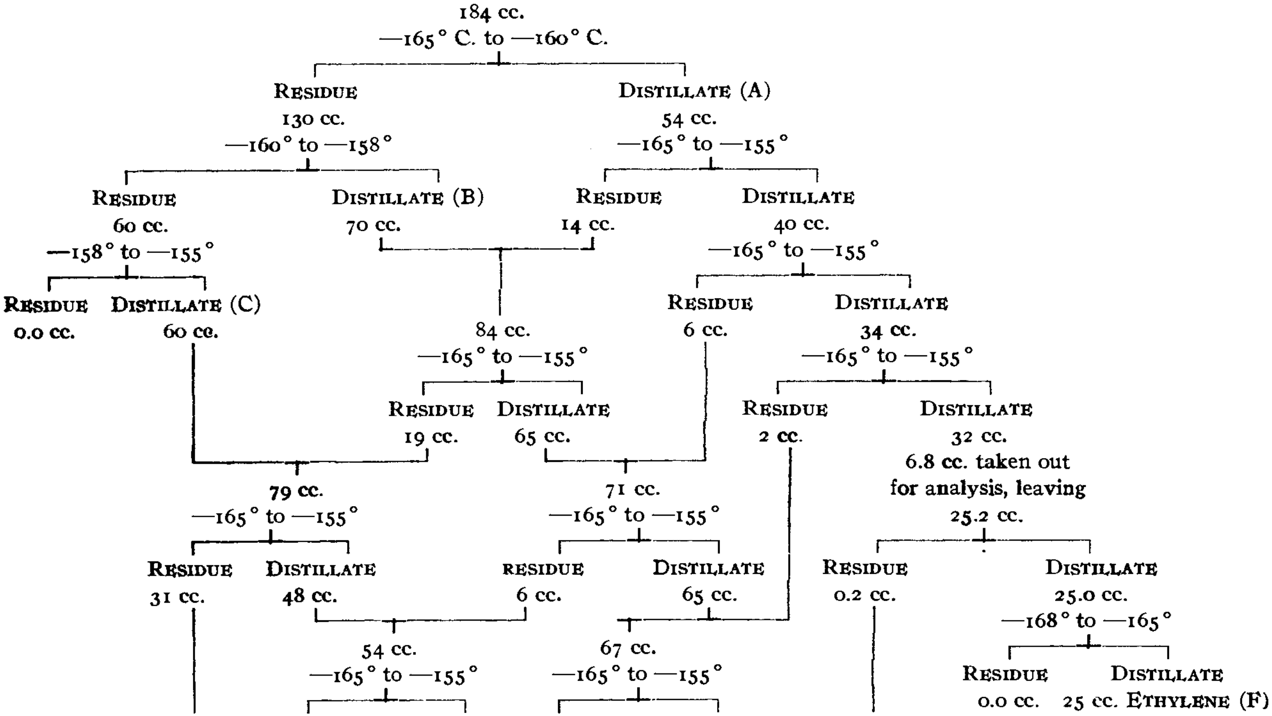
Separation of the Gases.—The two gases were mixed in equal proportions, 92 cc. of ethane and 92 cc. of ethylene. The fractionation was first tried at temperatures close to —170°, but so much ethylene was present, its removal so slow, and so much difficulty was experienced in maintaining a constant temperature for a long time, that higher temperatures and a

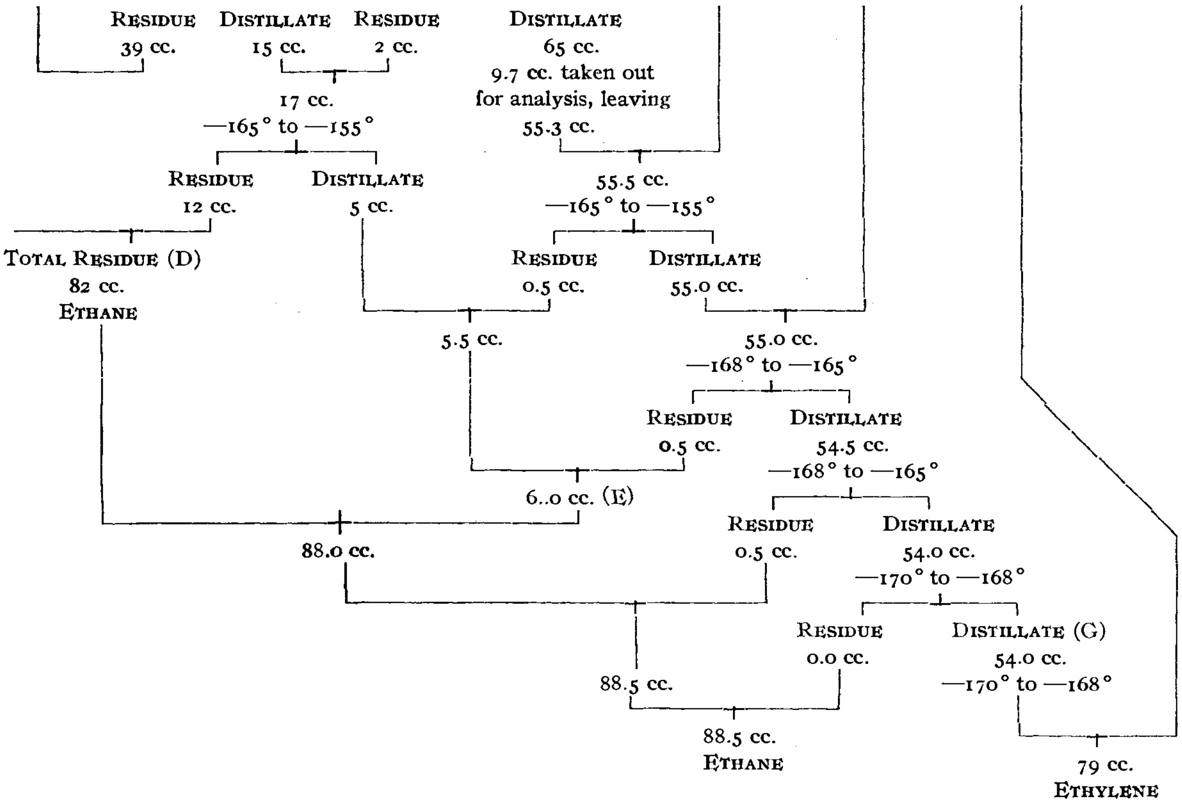
[1] THIS JOURNAL, **36**, 1537 (1914); **37**, 392 (1915).

[2] *J. Ind. Eng. Chem.*, **7**, 17–21 (1915).

[3] These vapor pressure measurements will be given in a subsequent paper.

FIGURE I.—FRACTIONAL DISTILLATION OF ETHYLENE AND ETHANE.




Residue
39 cc.
Distillate
15 cc.
Residue
2 cc.
Distillate
65 cc.
9.7 cc. taken out
for analysis, leaving
55.3 cc.
17 cc.
—165° to —155°
Residue
12 cc.
Distillate
5 cc.
55.5 cc.
—165° to —155°
Total Residue (D)
82 cc.
Ethane
Residue
0.5 cc.
Distillate
55.0 cc.
5.5 cc.
55.0 cc.
—168° to —165°
Residue
0.5 cc.
Distillate
54.5 cc.
—168° to —165°
6..0 cc. (E)
Residue
0.5 cc.
Distillate
54.0 cc.
—170° to —168°
88.0 cc.
Residue
0.0 cc.
Distillate (G)
54.0 cc.
—170° to —168°
88.5 cc.
88.5 cc.
Ethane
79 cc.
Ethylene

wider range was employed to first make an approximate separation. Hence the first fractionations were made at —160° to —155°, the second at —165° to —155°, the third at —168° to —165°, and the last ones at —170° to —168°.

At —165° to —160°.—There was obtained a distillate of 54 cc. This is marked distillate A on the diagram, Fig. 1. The residue from this distillation was refractionated at —160° to —158°. There was obtained 70 cc. of distillate (distillate B). The residue from this second distillation was refractionated at —158° to —155° and there was obtained 60 cc. of distillate (distillate C). No residue was left. It should be stated that at any of these temperatures all of the gas could be removed as a distillate in a comparatively short time by continuing the pumping long enough. The object was simply to divide the original portion into several fractions, each containing considerably more of one constituent than another, so that an excessive amount of gas would not have to be removed at lower temperatures, where the distillation proceeds more slowly.

Second Series of Fractionations.—The first distillate of 54 cc. (A) was refractionated at temperatures ranging from —165° to —155°. A distillate of 40 cc. was obtained. To the residue of 14 cc. there was added distillate B (70 cc.). This total (84 cc.) was distilled at —165° to —155°. The distillate amounted to 65 cc. and the residue to 19 cc. To the latter there was added distillate C (60 cc.). This total (79 cc.) was distilled at temperatures ranging from —165° to —155°. The distillate amounted to 45 cc. and the residue to 31 cc.

The foregoing illustrates the general procedure. All told, 18 fractionations were made. The diagram, Fig. 1, shows the various steps.

There was finally obtained 88.5 cc. of ethane and 79 cc. of ethylene. Two portions, one of 6.8 cc. and one of 9.7 cc. (total 16.5 cc.) had been removed during the fractionation as noted on the diagram, in order to determine by combustion analysis the purity of the fractions. In each case the separation was found to be incomplete. When this portion (16.5 cc.) is added to the final ethane and ethylene total (88.5 + 79 cc.) there results 184.0 cc., a quantity equal to the original amount.

Purity of the Fractions.—There are given below analyses of the various fractions to show their purity. They were examined by burning them with oxygen. The percentage of each constituent was calculated from the contraction and carbon dioxide produced.

According to the reaction, $C_2H_6 + 3.5O_2 = 2CO_2 + 3H_2O$, there result two volumes of CO_2 and a contraction of 2.5 volumes when ethane reacts with oxygen. It will be noted that the observed data correspond well with the theoretical equation.

TABLE I.

Analysis of Ethane.—Three of the following analyses were made of the residue marked *D* in the diagram. The total quantity of gas collected at this point was 82 cc. Three analyses were made. The data show analysis of ethane fraction.

The analysis in last column was made of the distillate marked (E) on the diagram (6 cc.):

Analysis No.	1. Cc.	2. Cc.	3. Cc.	4. Cc.
Gas taken for analysis	9.00	20.23	21.03	6.00
Oxygen added	63.47	83.37	97.82	75.43
Total volume	72.47	103.60	118.85	81.43
Volume after burning	49.84	53.22	66.57	66.43
Contraction	22.63	50.38	52.28	15.00
Volume after CO_2 absorption	31.77	12.81	24.45	54.71
CO_2 produced	18.07	40.41	42.12	11.72
Ethane calculated from contraction	9.05	20.15	20.91	6.00
Ethane calculated from CO_2	9.04	20.20	21.06	5.88

TABLE II.

ANALYSES OF THE ETHYLENE FRACTIONS.

Two of the following analyses were made of the ethylene distillate marked (F) on the diagram (25 cc. of distillate) and one of the distillate marked (G):

Analysis No.	1. Cc.	2. Cc.	Analysis of distillate G. Cc.
Sample taken	9.00	9.20	19.55
Oxygen added	47.10	43.76	73.25
Total volume	56.10	52.96	92.80
Volume after burning	38.45	34.87	53.81
Contraction	17.65	18.09	38.92
Volume after CO_2 absorption	20.70	16.70	14.82
CO_2	17.75	18.17	38.99
Ethylene calculated from the contraction	8.83	9.05	19.46
Ethylene calculated from the CO_2	8.87	9.08	19.50

According to the reaction $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$, there result 2 volumes of carbon dioxide and a contraction of 2 volumes when ethylene reacts with oxygen. The carbon dioxide and contraction in the foregoing analyses correspond with this reaction. In the case of analysis No. 1 the ethylene was not 100% pure, however, probably due to the intrusion of a trace of air. This point was not tested.

Conclusions.

Although the foregoing separation is complete within the error of making the analyses, the work involved is too tedious to be entirely satisfactory when the proportions of each constituent are present in considerable quantity. The ease of separation of gases whose boiling points are widely separated[1] is in sharp contrast to the separation recorded in this paper.

Constant temperatures were too difficult to maintain, and the removal of the gas by the pump too irregular at any particular temperature to

---

[1] *Loc. cit.*

obtain a ratio between the quantity of gases removed at different temperatures. As is invariably the case with liquids that tend to separate into two components, the less volatile one of the two (the ethane) was easier to obtain in a pure state. It is intended to repeat the work with a smaller percentage of one of the gases present than of the other and with the use of a thermostat such as was devised by F. Henning.[1] In another communication will also be shown the application of this method of separation to substances that are liquids at ordinary temperatures. In some separations the advantages over the use of high temperatures are: (1) The elimination of complicated still heads, and (2) the avoidance of loss by evaporation because high temperatures are not used. A different means of trapping the liquid had to be devised than that used in handling liquid gases.

All temperatures are in degrees centigrade. Details of the apparatus used are given in previous communications.

PITTSBURGH, PA.

[FROM THE CHEMICAL LABORATORY OF THE COLORADO AGRICULTURAL COLLEGE.]

ON THE OXIDATION OF ETHER.

BY R. M. ISHAM AND C. E. VAIL.

Received February 5, 1915.

It seems somewhat surprising to the authors that the subject of the oxidation of ether should have received but slight attention from the writers of our texts on organic chemistry. While the behavior of the alcohols and aldehydes on oxidation is considered in some detail, as representing important type reactions of these substances, the majority of our texts have nothing at all to say regarding the behavior of the closely related ethers. This is the more remarkable in consideration of the fact, which we shall show, that ether is very readily oxidized to aldehyde and acetic acid.

In the third American edition of Richter's "Organic Chemistry," Vol. I, p. 133, we find the statement that "When oxidized they (the ethers) yield the same products as their alcohols." Stoddard's "Introduction to Organic Chemistry," p. 73, states that "Oxidation (of ether) by means of nitric or chromic acid produces the same products as those obtained by the oxidation of alcohol—aldehyde and acetic acid." On the other hand, the 1907 edition of Roscoe and Schorlemmer's "Treatise on Chemistry," Vol. II, p. 1002, states that "Chromium trioxide dissolves without alteration......in pure ether," a statement which we were by no means able to verify. Aside from the above we have not, in a neces-

---

[1] *Z. Instrumentenkunde*, 33, 33 (1913). This thermostat was installed by the authors just before this article went to press. With it temperatures can be controlled within 0.03°.