

XLVIII.—*The Analysis of Mixtures of Hydrogen, Methane, and Ethane.*

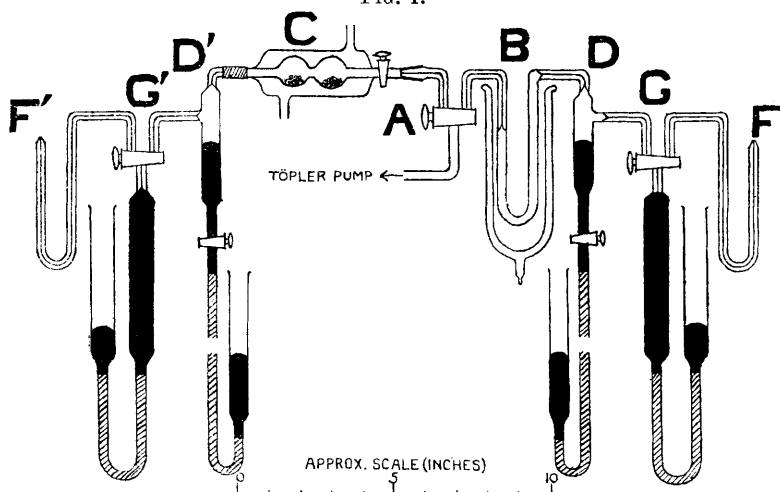
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THE principle of analysing gaseous mixtures by fractional distillation at low temperatures was applied by Burrell and Seibert (*J. Amer. Chem. Soc.*, 1914, **36**, 1537) for separating samples of natural gas into the individual hydrocarbons, and by Lebeau and Damiens (*Ann. Chim.*, 1917, **8**, 221) for the analysis of mixtures of hydrogen with the saturated hydrocarbons. Quite recently, Mulders and Scheffer (*Rec. trav. chim.*, 1930, **49**, 1057) have described a method of analysing mixtures of hydrogen, methane, and ethane, in which the mixture is separated into two portions by cooling with liquid air, each portion being then burnt separately over copper oxide. A similar method has been used by the present authors to determine methane and ethane in mixtures of these two gases (*Trans. Faraday Soc.*, 1931, **27**, 35), and the combination of this method with the palladium-absorption method for hydrogen is now described, since this affords a very simple means of analysing a mixture of the three gases. The method has the advantage that the two hydrocarbons can, if necessary, be exploded separately free from hydrogen. Their identity can therefore be established from the resulting C/A ratios (C = contraction after explosion, A = contraction after absorption by caustic potash), a point of special importance when unknown mixtures which may contain one or both of these hydrocarbons are being analysed. Moreover, the analyses to be described have been carried out on fairly small amounts of the mixture—about 5–10 c.c. in most cases—and are as accurate as those of Mulders and Scheffer, who used a total volume of some 30–40 c.c. for each analysis. The actual measurements of the quantities of gas before and after the various operations were made in a Bone and Wheeler apparatus of the usual type, in which the pressure of the gas at constant volume is observed, and the gas sample was transferred to and from the separation apparatus by means of small tubes inverted over mercury in a crucible.

Apparatus.—The form of separation apparatus is shown in Fig. 1. It consists of a Töpler pump connected by means of the three-way

stopcock A to (1) the U-tube B, which can be cooled by immersion in a vacuum vessel containing liquid air, for removal of the ethane, and (2) the palladium bulbs C, containing 2—3 g. of "oxidised" palladium sponge for removal of the hydrogen. The tubes B and C are connected respectively to the mercury traps D and D', the transferring pipettes G and G', and the bent capillary tubes F and F' dipping into mercury troughs. The hydrogen-absorption apparatus is similar to that described by Grice and Payman (*Fuel*, 1924, 3, 236), but improved by the introduction of the mercury trap and by the use of the steam-jacket for heating to 100°. The activity of the palladium is renewed from time to time by heating in a crucible in contact with air. A ground-glass joint was originally used in place

FIG. 1.



of the rubber connexion between C and D', but the latter, if well waxed, is just as satisfactory and renders the apparatus less susceptible to strain. The rubber tubing between the mercury traps and their reservoirs should, of course, be long enough to allow of the mercury level in the trap being adjusted when the apparatus is evacuated.

Analysis of a Mixture containing Hydrogen, Methane, and Ethane.—After being measured in the Bone and Wheeler burette, the gas sample is transferred (*via* the small inverted tube) through F' to the transferring pipette G. The apparatus is evacuated by means of the pump through A as far as the stop-cock of G, and the U-tube then immersed in liquid air by raising the Dewar vessel. A is then closed, and the sample transferred to B. After 5 mins., connexion is made to the pump again, and the uncondensed portion, consisting

of the hydrogen and the methane, pumped off and measured. The contraction gives the amount of ethane in the sample. Mulders and Scheffer (*loc. cit.*) noted that the condensed portions contained small amounts of dissolved methane, and found it necessary for exact work to carry out a second fractionation. We find, however, that quite accurate results can be obtained with one fractionation, probably owing to the use of smaller amounts of the gaseous mixture, and the increase in accuracy does not justify the extra time required for a second fractionation.

The palladium tube is then evacuated as far as G', and steam passed through the jacket of the tube C. The sample is introduced into C through F' and G', as in the former case, and allowed to remain in contact with the palladium at 100° for 15—20 mins. The steam is then replaced by cold water, and when the tube C is cold, the residual methane can be pumped off and measured. The difference between this reading and the previous one gives the amount of hydrogen. The amounts of the three constituents in the mixture can thus be determined by means of two simple operations: a complete analysis can be carried through after a little practice in 1½ hours. The following table shows the type of result obtainable. The mixtures were made up from the pure constituents. As a check,

C ₂ H ₆ , %.		H ₂ , %.		CH ₄ , %.	
Taken.	Found.	Taken.	Found.	Taken.	Found.
14.2	14.2	53.9	52.6	31.9	33.2
45.6	45.7, 46.1, 44.9	31.4	30.5, 31.3, 31.5	22.9	23.8, 22.6, 23.6
17.3	17.3, 17.1, 17.4	64.0	63.0, 63.6, 63.1	18.7	19.7, 19.3, 19.5
10.6	10.5	39.0	38.9	50.4	50.6
41.3	41.2, 41.8	40.0	40.4, 40.1	18.7	18.4, 18.1
40.4	39.7	42.2	42.6	17.4	17.7
29.2	29.5	54.4	53.6	16.4	16.9

the residual methane can be exploded, and the ethane condensed in the first stage can also be pumped off and exploded separately, but the results show that for ordinary accuracy and rapid working this is not necessary. In presence of nitrogen, however, explosion of the residual gas after the removal of ethane and hydrogen would be essential. Since the methane is determined by difference, it is subject to the largest error, the mean errors in the determination of the three constituents being: Ethane $\pm 0.8\%$, hydrogen $\pm 1.1\%$, and methane $\pm 2.6\%$. The percentage by volume of any constituent seldom differs from the calculated percentage by more than 1% of the total mixture, which is satisfactory in view of the small amounts of the gas used.

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