

This indicates that in very low phosphorus steels at least, the determination may be made as usual, provided the yellow precipitate is not allowed to stand more than two and one-half hours. Also in neutralizing with ammonia, no excess must be used or tungstic acid will precipitate with the ferric oxide and remain undissolved by the nitric acid added to clear the solution. But the tendency seems to be toward higher results.

#### Ferrotungsten

is usually analyzed by roasting, followed by solution, filtration, fusion, and evaporation with acid. The writer, with a sample containing 35.25 per cent. tungsten, obtained low results by this method (twenty-nine and thirty per cent.), doubtless because only a single fusion was made, but had no difficulty when using the same method as for tungsten steels, except that aqua regia was used for a solvent.<sup>1</sup> The ferrotungsten apparently could not be completely decomposed by this means. A bright metallic residue was left, consisting, however, of almost pure tungsten, and readily oxidizing to tungstic oxide by ignition after filtration. In this procedure the preparatory roasting of the ferrotungsten is, of course, unnecessary. The ferric oxide and other contamination seems to be variable; in nine determinations of five different ferrotungstens, it ranged from 0.28 per cent. to 1.60 per cent.

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### THE ABSORPTION OF METHANE AND ETHANE BY FUMING SULPHURIC ACID.<sup>2</sup>

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APPARENTLY one of the most firmly established facts has been that marsh-gas and its homologues are not acted upon either by fuming nitric or by fuming sulphuric acids. The indifference of methane and ethane to all reagents, especially to

<sup>1</sup> The metal being treated first with strong nitric acid and heated, and the strong hydrochloric acid then added by degrees.

<sup>2</sup> Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

fuming sulphuric acid, has been generally accepted as a fact and made a basis for the separation of the saturated from the unsaturated hydrocarbons in gas mixtures. Hempel, in his well-known book on gas analysis, states that no absorbent for methane is known; and a statement credited to Kolbe, and widely quoted, is to the effect that a mixture of fuming nitric and fuming sulphuric acids is without action on methane even at 150° C.

Apparently there has been but one observed instance of the absorption of a gaseous paraffin by fuming sulphuric acid. Orndorff and Young<sup>1</sup> found that propane made from isopropyl iodide by the copper-zinc couple was slowly soluble in cold fuming sulphuric acid, the absorption amounting to over fifty per cent. in fifteen days, the acid taking a deep red color. In a former communication<sup>2</sup> I have shown that the higher members of the marsh-gas series are acted upon by fuming sulphuric acid, the products being true sulphonic acids. The peculiar fact brought out during this work that each hydrocarbon sulphonated at its boiling-point, suggested the idea that the gaseous members of the series would be soluble in cold fuming sulphuric acid, and this has been found to be the case.

#### METHANE.

1. *From Methyl Iodide.*—The methane employed in the first series of experiments was made from pure methyl iodide by the copper-zinc couple of Gladstone and Tribe.<sup>3</sup> The gas produced by the reaction was washed by passing through fuming sulphuric acid and was then allowed to stand over fuming sulphuric acid for three hours to free it of alcohol vapors. A portion was then measured off with the measuring burette and the absorption determined by passing it into the usual glass bead absorption pipette, filled with fresh fuming sulphuric acid.

In using this apparatus it is easy to so manipulate that after the gas has all been transferred to the absorption pipette, the bend in the capillary tube of the latter shall be filled with the acid, thus forming an effectual seal which prevents the gas from coming in contact with rubber connections. These rubber con-

<sup>1</sup> *Am. Chem. J.*, 15, 261

<sup>2</sup> *Am. Chem. J.*, 20, 664.

<sup>3</sup> *J. Chem. Soc.*, 1884, 154.

nections were renewed frequently and the apparatus frequently tested for leaks with measured quantities of air. Two different absorption pipettes were used and any errors from leakage are highly improbable. The gas was each time run into a caustic potash pipette before a reading was made, in order to remove all acid vapors.

The data obtained in the first series are as follows :

| Time between readings. | Observed volume. cc. | Loss. cc. | Loss. Per cent. |
|------------------------|----------------------|-----------|-----------------|
| 0 .....                | 84.5                 | ....      | ....            |
| 30 min .....           | 84.4                 | 0.1       | 0.12            |
| 4 hours .....          | 79.0                 | 5.4       | 6.39            |
| 2 " .....              | 77.3                 | 1.7       | 2.01            |
| 12 " .....             | 74.0                 | 3.3       | 3.90            |
| 24 " .....             | 67.2                 | 6.8       | 8.04            |
| 5 days .....           | 56.2                 | 11.0      | 13.01           |
| 1 day .....            | 54.0                 | 2.2       | 2.60            |
| 2 days .....           | 49.9                 | 4.1       | 4.85            |
| 1 day .....            | 46.1                 | 3.8       | 4.48            |
| <hr/>                  |                      | <hr/>     | <hr/>           |
| 11 days                |                      | 38.4      | 45.40           |

The residue of 46.1 cc. was sealed into the pipette and allowed to stand over the fuming sulphuric acid during the three summer months. At the end of that time it had lost 22.2 cc., the residue amounting to only 23.9 cc. of the original 84.5 cc.—a total loss of 71.7 per cent. The color of the acid had changed from a light straw to a cherry-red and the absorption was still going on.

A comparison of the absorption figures in the above and in the following table shows apparent irregularities and discrepancies in the absorption at different periods for the same interval of time. This is easily accounted for by the variation in the barometer and thermometer on these different days, and for which variations no corrections were made when volumes were read, while the fact that the methane from methyl iodide shows a larger average daily absorption than that from natural gas is doubtless largely due to the much hotter weather prevailing during the former tests.

2. *From Natural Gas.*—The experiments with methane were repeated, using natural gas as the source of methane. The natural gas is piped to Lafayette from eastern Indiana, and analyzed as follows :

|                                            | Per cent. |
|--------------------------------------------|-----------|
| Hydrogen sulphide and carbon dioxide ..... | 1.80      |
| Oxygen .....                               | 0.70      |
| Heavy hydrocarbons .....                   | 0.50      |
| Carbon monoxide .....                      | 0.60      |
| Hydrogen .....                             | 0.55      |
| Nitrogen .....                             | 3.80      |
| Methane .....                              | 92.05     |
|                                            | 100.00    |

In a recent article by Prof. Phillips,<sup>1</sup> attention was called to the occurrence of hydrogen sulphide in a Canadian natural gas. This Indiana natural gas also contains large quantities of hydrogen sulphide, sufficient to give a pronounced odor to the gas and to rapidly precipitate a solution of lead acetate.

About 110 cc. of this natural gas were measured off and all constituents save nitrogen and methane removed by the ordinary method of gas analysis, using palladium sponge to remove hydrogen. The residue therefore consisted of ninety-six per cent. methane and four per cent. nitrogen.

The absorption was carried out as before described with the following results:

| Time between readings. | Observed volume.<br>cc. | Loss.<br>Per cent. |
|------------------------|-------------------------|--------------------|
| 0 .....                | 100.00                  | ....               |
| 16 hours .....         | 98.5                    | 1.5                |
| 7 " .....              | 98.0                    | 0.5                |
| 1 day .....            | 95.5                    | 2.5                |
| " .....                | 94.0                    | 1.5                |
| " .....                | 92.6                    | 1.4                |
| " .....                | 90.9                    | 1.7                |
| " .....                | 90.1                    | 0.8                |
| " .....                | 89.5                    | 0.6                |
| " .....                | 88.4                    | 1.1                |
| " .....                | 88.1                    | 0.3                |
| " .....                | 86.7                    | 1.4                |
| " .....                | 85.4                    | 1.3                |
| " .....                | 83.6                    | 1.8                |
| " .....                | 82.5                    | 1.5                |
| " .....                | 82.2                    | 0.3                |
| " .....                | 80.8                    | 1.4                |
| " .....                | 77.5                    | 3.3                |
| " .....                | 75.7                    | 1.8                |
| 17 days                |                         | 24.3               |

<sup>1</sup> This Journal, 20, 696.

That is, after remaining in contact with the fuming acid for seventeen days, a loss of 24.3 per cent. resulted,—an average daily absorption of one and four-tenths per cent. The residue was then sealed into the absorption pipette and allowed to stand three months during the winter. At the end of that time the total absorption amounted to 30.9 per cent.

## ETHANE.

The ethane employed was made from pure ethyl iodide by the copper-zinc couple, washed by passing through fuming sulphuric acid, and was then allowed to stand for eighteen hours over fuming sulphuric acid to free it of all alcohol vapors. The absorption was carried out in the manner described for methane with the following results :

| Time between readings. | Observed volume. cc. | Loss. cc. | Loss. Per cent. |
|------------------------|----------------------|-----------|-----------------|
| 0 .....                | 95.0                 | ....      | ....            |
| 1 day .....            | 91.3                 | 3.7       | 3.89            |
| " .....                | 84.7                 | 6.6       | 6.95            |
| " .....                | 79.5                 | 5.2       | 5.47            |
| " .....                | 75.8                 | 3.7       | 3.89            |
| " .....                | 70.2                 | 5.6       | 5.89            |
| " .....                | 65.0                 | 5.2       | 5.47            |
| " .....                | 61.1                 | 3.9       | 4.10            |
| " .....                | 57.3                 | 3.8       | 4.00            |
| " .....                | 53.2                 | 4.1       | 4.32            |
| " .....                | 48.2                 | 5.0       | 5.26            |
| " .....                | 43.0                 | 5.2       | 5.47            |
| " .....                | 39.5                 | 3.5       | 3.68            |
| " .....                | 36.2                 | 3.3       | 3.47            |
| " .....                | 32.0                 | 4.2       | 4.42            |
| " .....                | 28.0                 | 4.0       | 4.21            |
| 15 days                |                      | 67.0      | 70.5            |

In fifteen days, therefore, the absorption of ethane amounted to 70.5 per cent.,—an average daily absorption of 4.7 per cent. The residue was sealed into the pipette and allowed to remain in contact with the fuming acid for three months. At the end of that time the total absorption amounted to 88.3 per cent. As may be seen by comparison, the absorption of ethane is much more rapid than that of methane. Some oxidation results during this absorption, as carbon dioxide and sulphur dioxide are always produced. From the change in color of the acid it is probable that a sulphonic acid is also formed.

These results, establishing as they do the fact that methane and ethane are soluble in fuming sulphuric acid, are not without importance in their bearing toward gas analysis. A number of experiments were tried to determine the amount of absorption of each gas that took place in short intervals of time. After twenty-five per cent. of the methane obtained from natural gas had been absorbed, the residue was tested by measuring its absorption each hour. The results showed this absorption to be very slight, less than one-tenth cc. per hour. In the case of ethane, however, after over sixty per cent. had been absorbed, a similar series of experiments gave an average hourly absorption of 0.25 cc. equivalent to 0.60 per cent. of the ethane present.

In ordinary technical gas analysis, therefore, when the gas contains methane but no ethane, the absorption in the fuming sulphuric acid could be allowed to continue for an hour if necessary without much danger of serious error. But if ethane is present, fifteen minutes is the probable maximum of safety, and in any case the safest course to follow, especially in the case of an unknown gas, would be to shorten the time of contact with fuming sulphuric acid to the lowest possible limit.

LAFAYETTE, IND., October, 1898.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

## THE VELOCITY OF THE REACTION BETWEEN SILVER ACETATE AND SODIUM FORMATE. A REACTION OF THE THIRD ORDER.<sup>1</sup>

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### I. OBJECT OF THE INVESTIGATION.

THE investigations hitherto made of the velocities of those reactions in which two or more molecules of a substance enter have not yielded results of a general character. In many cases the velocity has been found proportional simply to the concentration of the substance, while in others it has been found proportional to that power of its concentration which corresponds to the number of its molecules entering into the reaction, as theoretical considerations would appear to demand. Thus, for ex-

<sup>1</sup> Read before the Boston meeting of the American Chemical Society, August 25, 1898.