put on, and the whole allowed to remain in the balance case for twenty minutes before weighing.

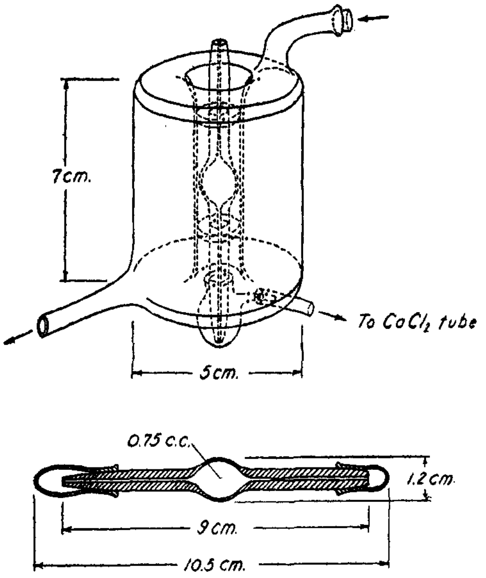

Fig. 3.

The density is then calculated as follows:[20] If the pycnometer contains v_1 cc. (w_1 g.) of water at temperature t_1 and v_2 cc. (w_2 g.) at temperature t_2 and v_3 cc. (w_3 g.) of liquid, of which the density, d, is required, at temperature t_3 and if the coefficient of linear expansion of the glass of which the pycnometer is made is α, then

$$v_2 - v_1 = 3\alpha v_1\,(t_2 - t_1)$$

and

$$v_3 - v_1 = 3\alpha v_1\,(t_3 - t_1)$$

$$\therefore \quad v_3 - v_1 = (v_2 - v_1)\,\frac{(t_3 - t_1)}{(t_2 - t_1)}$$

$$= k(t_3 - t_1) \text{ where } k = \frac{(v_2 - v_1)}{(t_2 - t_1)}$$

$$\therefore \quad d_4^{t_3} = \frac{w_3}{v_3} = \frac{w_3}{v_1 + k(t_3 - t_1)}$$

Summary

1. A convenient apparatus is described for the production of deuterium and reduction of organic compounds with this gas.

2. Dimethyl acetylene dicarboxylate was reduced with deuterium to dimethyl succinate-α-d_2,-α'-d_2 and from it by hydrolysis succinic-α-d_2,α'-d_2 acid was obtained. This latter was converted by means of phosphorus oxychloride to succinic-α-d_2,α'-d_2 anhydride.

3. The analyses, boiling points, melting points, densities and indices of refraction were determined and compared with those of the hydrogen analogs.

4. An apparatus for determining the density of solids which melt without decomposition is described.

5. It has been demonstrated that, under the conditions used, the replacement of deuterium by hydrogen, if it takes place at all, is a very slow reaction.

URBANA, ILLINOIS

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[20] *Cf.*, Reilly and Rae, "Physico-Chemical Methods," 1933, p. 337.

[CONTRIBUTION FROM SUN OIL COMPANY RESEARCH LABORATORY]

The Freezing Point and Boiling Point of Propane[1]

BY MILDRED M. HICKS-BRUUN AND JOHANNES H. BRUUN

1. Introduction

Although the freezing points of the pure normal hydrocarbons with an odd number of carbon atoms are, in all cases, considerably lower than those of the even-numbered compounds of the same series, the generally accepted value, −189.9°, given for the freezing point of propane seems unduly low. It is not only lower than that of its lower even-numbered homolog, ethane (f. p. −172.0°), but also is lower than that of methane (f. p. −184°). For this reason it was suspected that perhaps the value found in the literature for the freezing point of propane was not correct and that a higher value might be obtained by intensive purification of the propane, and improved technique in the determination of its freezing point.

Furthermore, the value −189.9°, reported by Maas and Wright[2] was determined by carefully raising and lowering the temperature of a bath in which was suspended a sealed glass bulb that contained less than 2 ml. of propane. These authors state that difficulty was experienced with supercooling, but that this effect was minimized by freezing the sample more than one time, successively. However, in a procedure such as that given above, it was not the temperature of the

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[1] Presented before the Division of Petroleum Chemistry at the 91st meeting of the American Chemical Society, Kansas City, Missouri, April 13-17, 1936.

[2] Maas and Wright, THIS JOURNAL, 43, 1098-1111 (1921).

crystallizing liquid hydrocarbon, but that of the surrounding bath which was actually measured. Furthermore, the size of the sample was very small compared to that of the bath. Hence the effect of the heat given off during the crystallization of the propane, *i. e.*, 16.2 calories per gram[3] was largely dissipated. Consequently the value which was obtained for the freezing point of the propane would be expected to appear lower than its true value.

In view of these facts, it seemed worth while to make time–temperature cooling curves[4] on larger volumes of fractions obtained from the careful purification of the best commercial propane.

Many of the available data on the physical constants of propane have been summarized in a recent paper by Cox.[5] The nine values given for the boiling point vary over a range of seven degrees centigrade. Hence, it seemed desirable to determine this constant also.

2. Apparatus

Since the freezing point of propane was found by Maas and Wright[2] to be below the boiling point of liquid air at atmospheric pressure, it was necessary to lower the temperature of the liquid air-bath by reducing the pressure above it. By means of a vacuum pump, a bath temperature as low as −215° could be maintained.

The use of a temperature as low as −200°, however, necessitated freezing the propane itself under vacuum to protect it from errors due to the condensation of oxygen from the air and its subsequent solution in the propane. This was done by a specially designed freezing tube which is shown in Fig. 1. The correct immersion depth for the thermoelement was established empirically.[6] The total volume of propane used in the tube was 13.5 ml.

The boiling tube was constructed similar to the freezing tube, but with a larger diameter. The propane sample was protected from atmospheric moisture by means of a "Dehydrite" drying tube. The temperature of the surrounding bath was kept at −35°, which permitted uniform boiling at a moderate rate.

The thermoelement was a five-junction unit which was constructed from No. 30 constantan and No. 36 copper wire. It was calibrated at the National Bureau of Standards and the values for the temperature scale were certified to 0.05°.

3. Experimental Methods and Results

The starting material for the present investigation consisted of a commercial sample of propane of the highest obtainable purity (presumably 99.99%). While the amount of unsaturateds in this sample was undetectable by the best available analytical methods and while the distillation curve obtained in a Podbielniak column[7] indicated that the sample was of the highest purity, it was felt that for this particular case these tests could not be relied upon as a final criterion of purity. It was conceded that traces of methane and ethane as well as small amounts of isobutane could be present without being detected by means of ordinary analytical tests. For this reason the propane was subjected to further careful purification. Three liters of the propane were shaken for ten hours under pressure at 70° with chlorosulfonic acid in lead-lined steel bombs. The chlorosulfonic acid is known to react with compounds containing tertiary carbon atoms,[8] such as isobutane, as well as olefins. This treatment was followed by a treatment with sodium hydroxide and by distillation. The distillation was carried out in a specially designed twenty-plate, all-glass still to be described later. Three charges of about 900 ml. each were made into this still and the middle fractions from these distillations were combined and subjected to another distillation in the same still. As a result of these distillations, all of which were done at atmospheric pressure, two 150-ml. fractions of purified propane were obtained.

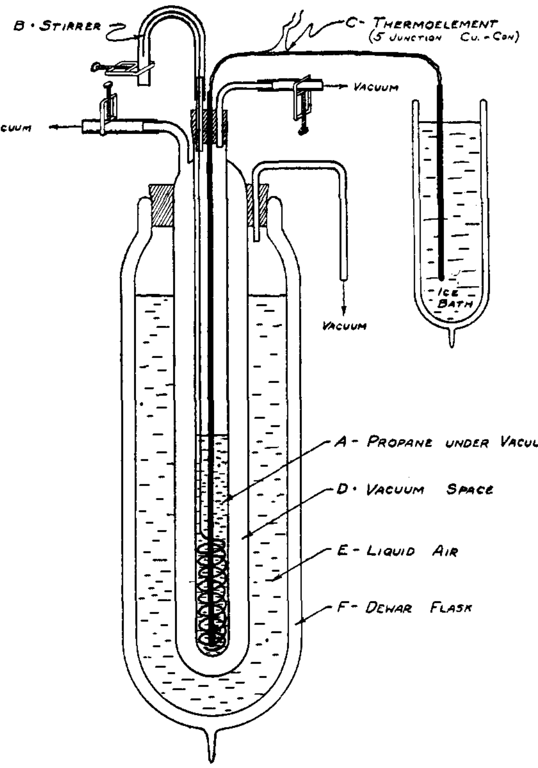

Fig. 1.—The freezing tube.

Time–temperature cooling curves for the original propane together with the best fraction obtained from the above purification are shown in Fig. 2. The purified sample had a freezing point of −187.1 ± 0.1 or 0.6° higher than that of the original propane.

The boiling point of the purified fraction of propane was found to be −42.17 ± 0.05° at 760 mm.

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[3] Parks and Todd, *Ind. Eng. Chem.*, **21**, 1235 (1929).

[4] Hicks, *Bur. Standards J. Research*, **2**, 483 (1929).

[5] Cox, *Oil and Gas Journal*, **33**, 16 (1935).

[6] Roser and Wenzel, *Bur. Standards J. Research*, **14**, 256 (1935).

[7] Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177-188 (1931).

[8] Aschan, *Ber.*, **31**, 1801 (1898).

Another interesting difference was observed between the purified fractions of propane and the original, so called "pure," commercial grade. The latter had a pronounced odor, while no odor at all could be detected for the purified samples.

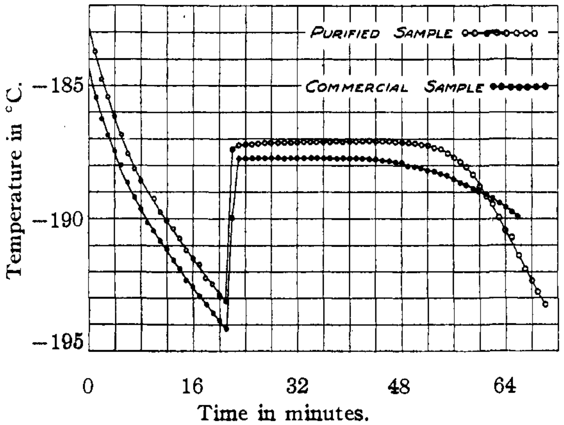

Fig. 2.—Time–temperature cooling curves of treated and untreated samples of commercial propane.

4. Discussion

The freezing points of the original fraction and the fraction obtained by purification treatment are both considerably higher than the previous published value[2] but still they are not as high as that of methane. Many check runs were made for all of the data given. In no case did the values obtained vary more than 0.2°.

Since the freezing point of the commercial sample was found to be 0.6° lower than that of the purified propane, a theoretical calculation based upon this value and upon the Parks and Todd[3] value, 16.2 calories per gram for the heat of fusion, discloses the fact that the purity of the original ("pure") sample of propane was only 97.1 (±0.5%) mole per cent.

The freezing point reported by Maas and Wright is −189.9° or 2.8° below that obtained in this Laboratory. This could indicate that their propane was 86.9 (±0.5%) mole per cent. pure. However, it is considered likely that a large part of the discrepancy in freezing point resulted from the difference in freezing technique used and was not wholly due to impurities in the propane.

The value −42.17 ± 0.05° which was obtained in the present investigation for the boiling point of the purified propane is in substantial agreement with the value −42.12° which Dana and his co-workers[9] determined by means of a platinum resistance thermometer. It is slightly higher than the values, −42.5 and −42.6°, which Cox[6] cited as calculated from the vapor pressure data of Young[10] and Lacey and his co-workers,[11] respectively.

Summary

A sample of pure propane has been prepared by treatment of high grade commercial propane with chlorosulfonic acid and by subsequent fractional distillation at atmospheric pressure. The experimental value found for the freezing point of propane was −187.1 ± 0.1°, which indicates that although the generally accepted value for this constant is nearly three degrees too low, the present value is also lower than that of methane.

NORWOOD, PENNA. RECEIVED FEBRUARY 11, 1936

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[9] Dana, Jenkins, Burdick and Timm, *Refrig. Eng.*, **12**, 387–405 (1926).

[10] Young, *Proc. Irish Acad.*, **38**, 65–92 (1928).

[11] Sage, Schaafsma and Lacey, *Ind. Eng. Chem.*, **26**, 1218 (1934).