

[CONTRIBUTION FROM THE SUN OIL COMPANY, EXPERIMENTAL DIVISION]

Isolation of 2,2-Dimethylbutane from Natural Gas and Determination of its Physical Properties¹

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1. **Introduction.**—In previous publications,^{2,3} the authors have reported the isolation of pure samples of four isomeric hexanes: *n*-hexane b. p. 68.7°, 3-methylpentane b. p. 63.2°, 2-methylpentane b. p. 60.19° and 2,3-dimethylbutane b. p. 57.93°. While the fifth of the isomeric hexanes, 2,2-dimethylbutane b. p. 49.7° has been prepared synthetically,⁴⁻⁸ it seems that no one has ever isolated this compound in a pure condition from any naturally occurring product such as petroleum or natural gas. In our recent investigation⁹ of the 55–66° cut from Clendenin Gas Field in West Virginia, we found that approximately 7.4% of this cut, when fractionated in our 100-plate bubble cap stills,^{9,10} distilled between 38 and 58°. A subsequent refractionation of this low boiling cut resulted in a definite flat break between 49 and 50° of the distillation curve. The refractive index of the material distilling within this range, however, was too high to correspond to 2,2-dimethylbutane alone and it was concluded that it was mixed with cyclopentane, b. p. 49.2°. Because of the relatively small amounts of this fraction available in the 55–66° cut we were unable at that time to isolate the missing isomer of hexane in a pure condition. The distillation served to indicate, however, that a complete separation might be possible provided the investigation was started with larger amounts of the material boiling as near 49–50° as possible. Inasmuch as the isolation of the 2,2-dimethylbutane would supply complete data on the natural occurrence of the isomeric hexanes in petroleum, it was thought advisable to complete this work.

2. **Raw Material Used.**—From the Viking Distributing Company, 20 gallons (76 liters) of the 38–55° cut from the

natural gas originating in the Clendenin Field in West Virginia has been obtained. This cut was reported to be present to the extent of 18 gallons (68 liters) of liquid per 1000 cubic feet (28,317 liters) of the natural gas measured at a pressure of 14 pounds per square inch (1 atm.).

3. **Isolation of the 2,2-Dimethylbutane.**—About 37 liters of the raw material was extensively fractionated in two semi-automatic all-glass stills having bubble cap columns of 100 plates each and still pots of 3 and 5 liters capacity. The reader is referred to previous publications for a complete description of these stills.^{9,10}

The first distillation consisted of 11 separate runs with charges of either 2500 or 4500 ml. each. The stills were operated at a reflux ratio of about 20:1 and the distillates were collected at a rate of about 0.8 ml. per minute between 26 and 40° and of about 0.1 ml. per minute in the range between 40 and 50°. The temperature–volume relationships of these runs were exactly identical and are given in Fig. 1. As shown in this figure, over 50% of the raw material consisted of *n*-pentane (boiling point 36°) while the 2,2-dimethylbutane fractions (refractive index, n_D^{20} averaged 1.380) represented about 10% of the original 38–55° cut. It is noted that the true boiling range of the 38–55° commercial cut varied from about 26 to above 60°.

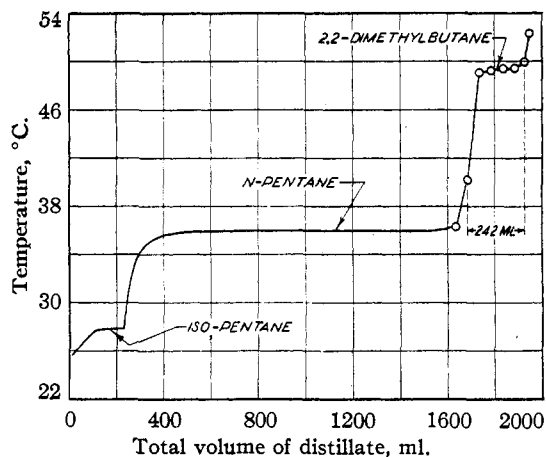


Fig. 1.—First distillation of the raw material.

For the second distillation all of the cuts from the first distillation having boiling ranges of 40–50° were combined and recharged into one of the 100-plate stills which in this case was operated at about 75:1 reflux ratio while the distillate was being collected at a rate of 0.1 ml. per minute. During this run about 80% of the charge distilled between 49.2 and 49.8°.

The third distillation consisted in mixing all fractions from the second distillation boiling at about 49.7° and having refractive indices corresponding to that of the 2,2-dimethylbutane and then subjecting them to a final fractionation in the 100-plate still. The final charge consisted

(1) Paper presented before the Petroleum Division of the American Chemical Society Meeting in Boston, Mass., September, 1939.

(2) (a) J. H. Bruun and M. M. Hicks-Bruun, *Bur. Standards J. Research*, **5**, 933–942 (1930); (b) J. H. Bruun and M. M. Hicks-Bruun, *ibid.*, **6**, 869–879 (1931).

(3) J. H. Bruun, M. M. Hicks-Bruun and W. B. Mason Faulconer, *THIS JOURNAL*, **59**, 2355–2360 (1937).

(4) J. Timmermans, *Bull. soc. chim. Belg.*, **31**, 389 (1922).

(5) H. v. Risseghem, *ibid.*, **31**, 65 (1922).

(6) J. Smittenberg, H. Hoog and R. A. Henkes, *THIS JOURNAL*, **60**, 17 (1938).

(7) C. R. Noller, *ibid.*, **51**, 594 (1929).

(8) P. L. Cramer and M. J. Mulligan, *ibid.*, **58**, 373 (1936).

(9) J. H. Bruun, *Ind. Eng. Chem., Anal. Ed.*, **8**, 224 (1936).

(10) J. H. Bruun and W. B. Mason Faulconer, *ibid.*, **9**, 192 (1937).

TABLE I
 PHYSICAL CONSTANTS OF 2,2-DIMETHYLBUTANE

	Bruun, Hicks-Bruun Faulconer ^a	H. v. Risseghem ^b	Cramer and Mulligan ^c	J. Timmermans ^d	J. Smittenberg H. Hooge R. A. Henkes ^e	A. v. Grosse ^f
Boiling point, °C.	49.72 ± 0.03	49.73 ± 0.02	49.80 to 49.82	49.7 ± 0.02	49.7
Freezing point, °C.	-98.7 ± 0.2 ^g	-98.2	-98.2	-100.5
1st transition point, °C.	-99.7 ^g (?)
2nd transition point, °C.	About -146 ^g	About -146
Specific gravity	d^{20}_4	0.6494	0.6491	0.6493
	d^{25}_4	.64475
	dd/dt	.00093
Refractive index	n^{15}_D	1.37518
	n^{20}_D	1.3689	1.3692	1.3691
	n^{25}_D	1.36615
	dn/dt	0.00055

^a Present investigation. ^b *Bull. soc. chim. Belg.*, **31**, 65 (1922). ^c *THIS JOURNAL*, **58**, 373 (1936). ^d *Bull. soc. chim. Belg.*, **31**, 389 (1922). ^e *THIS JOURNAL*, **60**, 17 (1938). ^f *U. O. P. Bull.* 219, 1938, p. 21. ^g *In vacuo*.

of only 760 ml. of material and the total boiling spread of this charge was found to be 0.1°. The two best samples of about 40 ml. each obtained from the upper end of this distillation had a boiling spread of 0.01° in the 100-plate column.

4. Determination of the Physical Constants of 2,2-Dimethylbutane.—The freezing point, boiling point, the refractive index and the specific gravity of the isolated 2,2-dimethylbutane were determined by using the same apparatus and technique as that employed for the other isomeric hexanes.³

The boiling point was determined by means of a Cottrell boiler and the conventional corrections have been applied to the value given in Table I. A Valentine Abbe type refractometer which reads to the fifth decimal place was used to determine the refractive index. Its calibration was checked with pure distilled water and pure *n*-hexane.

The freezing point was determined under vacuum. The 25-ml. sample was placed in a small unsilvered Pyrex vacuum flask, of which the vacuum chamber was equipped with a manometer and stopcock. This arrangement enabled the operator to vary the rate of cooling by changing the vacuum around the sample. A stirrer and a 5-junction copper-constantan thermocouple were provided in order to stir and to read the temperature of the sample. The thermocouple was calibrated by the National Bureau of Standards. The vacuum sample tube was surrounded by a bath of liquid nitrogen which was contained in an unsilvered Pyrex thermos flask.

The specific gravity was determined in a 5-ml. pycnometer specially designed and loaned by S. S. Kurtz, Jr., of the Development Division of this Company. The values were corrected for buoyancy effect and are believed to be accurate to the fourth decimal place.

All of the final corrected values are listed in Table I, together with the best available data on the synthetic hydrocarbon.

5. Discussion of the Results.—From the close agreement of the physical constants, as well as the freezing behavior, it has been concluded that a very pure sample of 2,2-dimethylbutane

can be obtained from petroleum by efficient distillation alone.

In Table I, the physical constants are given for the best fraction of 2,2-dimethylbutane which has been obtained in this Laboratory. For direct comparison, the best values from the literature of the physical constants of the pure synthetic hydrocarbon are also included. It can be seen that they are in close agreement with the best of the values except for the freezing point. The freezing behavior proved to be very interesting. The best values found in the literature were those of Timmermans⁴ and of van Risseghem,⁵ which were both -98.2°, while Smittenberg, Hoog and Henkes⁶ found -100.5° and a transition point of -146°. The latter authors were unable to obtain a flat horizontal portion of the curve during the time that freezing took place. They concluded that the substance was pure but the crystallization was inadequate to maintain the temperature at a constant point over the period of freezing.

In the present investigation, in which 25 ml. of 2,2-dimethylbutane was frozen *in vacuo* in concentric transparent vacuum flasks, certain unusual freezing characteristics could be observed. In a normal freezing process supercooling occurs, followed by the formation of white crystals and a horizontal plateau on the time-temperature cooling curve. From the curve in Fig. 2, it can be seen that the first white crystals appeared and a flat portion was obtained about one degree below the point at which the material began to solidify. Thus at -98.7 ± 0.2°, the liquid, without the change in viscosity, which usually occurs if it becomes a glass, began to solidify but remained

transparent. By the time the temperature had dropped one degree, the 2,2-dimethylbutane was almost solid, but still clear. At this point small groups of white crystals began to form and spread rapidly throughout the mass, while the temperature became stationary. This behavior could be duplicated, although it sometimes happened that the white crystals began to form directly at about -99° . In such cases, the temperature did not remain stationary but fell gradually. This behavior gave a time-temperature curve such as that described by Smittenberg, Hoog and Henkes.⁶ Whether the first solidification to a transparent mass, with the subsequent change to a white crystalline mass, is evidence of a definite transition point or merely that the first crystals are exceedingly small has not been established. As the main purpose of this investigation has been only to isolate the 2,2-dimethylbutane in a pure condition, no further work has been done on this point. However, due to the rapid change in temperature when the material began to freeze, it is somewhat difficult to establish conclusively the exact temperature of the initial freezing point. The heat of fusion of 2,2-dimethylbutane is 111 cal.₁₅^o per mole,¹¹ which is very low. Calculated from this value, if the freezing point of -98.2° found by Timmermans⁴ and van Risseghem⁵ is correct and the one for the present sample is 0.5° lower, the purity of the latter is still 99.91%.

A transition point of about -146° has been reported.^{6,11} Stull measured the heat of transition at this temperature and found it to be 1095 cal.₁₅^o per mole¹¹ or about ten times the heat of fusion. In the present sample, considerable supercooling (about 20°) occurred before the transition took place. However, the transition point of -146° has been confirmed in this Laboratory.

6. Percentage of the Various Isomeric Hexanes in the Natural Gas.—In Table II, the authors have listed the approximate relative quantities in which the isomeric hexanes are present in the natural gas.

(11) D. R. Stull. *THIS JOURNAL*, **59**, 2726-2733 (1937).

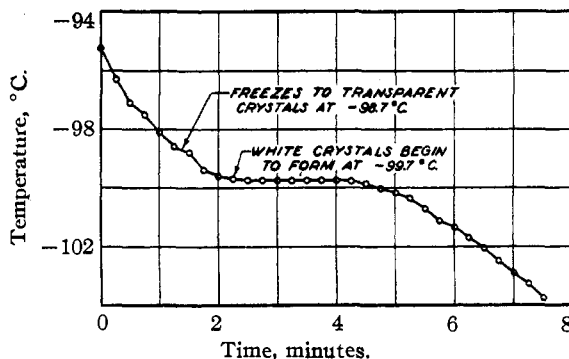


Fig. 2.—Time-temperature cooling curve of 2,2-dimethylbutane.

TABLE II
CALCULATED AMOUNTS OF ISOMERIC HEXANES IN NATURAL GAS

Compound	Boiling point, °C.	Minimum amount present, ml. of liquid per cu. m. natural gas
2,2-Dimethylbutane	49.72	168
2,3-Dimethylbutane	57.93	74 ^s
2-Methylpentane	60.19	420 ^s
3-Methylpentane	63.2	196 ^s

Summary

2,2-Dimethylbutane, the only isomeric hexane that has never been separated from natural sources, has been isolated in a pure condition from natural gas. A careful study of the freezing behavior of 2,2-dimethylbutane has revealed that the compound froze to transparent solid crystals at -98.7° without resulting in a flat portion in its time-temperature cooling curve. One degree lower at -99.7° white crystals began to form and a horizontal plateau appeared on the freezing curve. No attempt has been made to establish whether this behavior is due to the initial formation of very fine crystals or to a definite transition point between two crystal modifications.

The isolated compound is present in natural gas to the extent of 168 ml. per cu. m., and is thus next to 2,3-dimethylbutane, the least predominant isomer of hexane.

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