XCII.—*Separation of Normal and Iso-heptane from American Petroleum.*

By FRANCIS E. FRANCIS, B.Sc., Ph.D., and SYDNEY YOUNG, D.Sc.,
F.R.S.

AN attempt made by one of us to separate the heptanes from American petroleum by fractional distillation, after removal of toluene by treatment with a mixture of nitric and sulphuric acids, was unsuccessful, owing to the presence of polymethylene compounds in the petroleum.

It seemed possible, however that, by the action of bromine, the polymethylene compounds might yield higher bromine derivatives more readily than the paraffins, and that the heptylic monobromides might thus be obtained in a pure state. The bromides could then be reduced to the corresponding paraffins by means of nascent hydrogen.

A preliminary experiment with about 90 grams of the fractionated petroleum, boiling between 98.65° and 99.65° and containing chiefly normal heptane and methylhexamethylene, gave promising results, a small quantity of a bromide boiling at about 93° under a pressure of 70 mm. being obtained.

It was then decided to brominate a large quantity of the mixed heptanes—containing a considerable amount of methylhexamethylene, a little hexamethylene, and possibly some dimethylpentamethylene.

In the first experiment, 900 grams of bromine were gradually added to 760 grams of the petroleum (b. p. $96.5-102^{\circ}$), small quantities of aluminium bromide being introduced from time to time. In this case, however, higher bromides of both the paraffins and polymethylene compounds were chiefly formed, for, on distillation, 605 grams of unaltered petroleum were recovered, and no monobromides could be isolated from the residue.

The second bromination was carried out without the use of aluminium bromide, and the temperature was raised only just sufficiently for the action to take place. In this case, 517 grams of hydrocarbon (b. p. 95—101°), and 850 grams of bromine yielded 730 grams of bromides and 180 grams of unaltered petroleum. By repeated fractionation under reduced pressure (70 mm.), 87·5 grams of monobromide, boiling at 93—94·5° were obtained. The bromide was then reduced in alcoholic solution with a zinc-copper couple, small quantities of saturated hydrochloric acid being added from time to time. The paraffin, separated with water, washed, dried, and distilled, gave 48·3 grams of heptane and 17·5 grams of unaltered bromide. The heptane boiled mostly at 98°, and its sp. gr. was 0·70393 at 0°/4°. After treatment with a mixture of sulphuric and nitric acids, this was reduced to 0·70238.

A third quantity of petroleum (760 grams), richer in isoheptane (b. p. 93·5—102°), was then brominated at a higher temperature, the unaltered hydrocarbon being distilled off from time to time, and again heated with bromine. The bromides were then distilled under reduced pressure and the monobromides were fractionated fourteen times with the 12 column dephlegmator under a pressure of 70 mm.

Normal heptylic bromide was obtained with constant boiling point, 93·0°, under 70 mm. pressure. Its sp. gr. at 0°/4° was 1·1577.

Isoheptylic bromide was separated in a fairly pure state; b. p. 82—84·2°, mostly at 83—84°, under a pressure of 70 mm. When distilled from a bulb with short still-head, most of it came over at 84°. The sp. gr. was 1·1667 at 0°/4°.

The normal heptylic bromide was reduced in the same manner as before, and the normal heptane, after one distillation, boiled at 98·35—98·5°; the sp. gr. was 0·70314.

The whole of the normal heptane was then heated with fuming nitric acid, washed with caustic soda, then with water, dried over phosphorus pentoxide, and distilled with the 12-column dephlegmator. The boiling point was now 98·2—98·5° and the sp. gr. 0·70186.

It is probable that the heptane still contained a very small quantity of nitro-compound, which would raise its specific gravity, but it was evidently very nearly pure. The critical consonants were then determined with the portion coming over between 98·25° and 98·45°, also the vapour pressures and specific volumes at a few temperatures. The results are given in the table below, together with the corresponding constants determined with Dr. Thorpe's well known specimen of normal heptane from *Pinus sabiniana*. In the calculation of the volumes of a gram, the sp. gr. at 0° was taken to be 0·70048, and not 0·70168.

	Normal heptane from	
	Petroleum.	<i>Pinus sabiniana.</i>
Boiling point.....	98·25—98·45°	98·43°
Specific gravity 0°/4°	0·70186	0·70048
Critical temperature.....	267·0°	266·85°
„ pressure	20550 mm.	20430 mm.
„ volume of a gram	4·261 c.c.	4·266 c.c.
Vapour pressure at 130°	1773	1753
„ „ 240	13825	13790
„ „ 260	18530	18470
Volume of a gram of liquid at 130°	1·717 c.c.	1·7176 c.c.
„ „ „ 240	2·390	2·394
„ „ „ 260	2·882	2·895
Volume of a gram of saturated vapour at 240° ...	13·45 c.c.	13·43
„ „ „ 260 ...	7·796	7·77

It will be seen that the critical temperatures and the volumes of a gram agree very well indeed, but the pressures show somewhat greater differences.

The isoheptylic bromide was similarly reduced, and the paraffin was treated for a short time with fuming nitric acid, but it was rapidly attacked and the quantity was so seriously diminished that no fractionation was possible, and it could only be once distilled.

The boiling point was 89·9—90·4° and the sp. gr. 0·70670 at 0°/4°.

Thorpe determined the boiling point and specific gravity of a specimen prepared by the action of sodium on a mixture of ethylic and amylic bromides and obtained the values 90·3° and 0·69692 at 0°/4°.

There can be little doubt that the isoheptane from petroleum contained some nitro-compound, which would raise the specific gravity. From its boiling point, it would appear to be identical with Thorpe's specimen.

UNIVERSITY COLLEGE,
BRISTOL.