

THE CHEMISTRY OF THE HEPTANE SOLUTION.

BY EDWARD KREMERS.

3. PURIFICATION OF HEPTANE AND ITS PHYSICAL CONSTANTS.

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Possibly of no hydrocarbon of the methane series have the physical constants been determined with greater satisfaction than those of normal heptane by Thorpe in 1879. The special reasons for this are:

1. The *n*-heptane on which Thorpe made his observations was the product of a plant which apparently does not produce either isomers or homologues of this hydrocarbon.

2. Of the purified material he had a sufficient amount—about seven liters—to make certain of its purity by the constant boiling point of practically the entire amount.

This is in such striking contrast to the materials used in the determination of the physical constants of other hydrocarbons of this series, that it seemed desirable to make doubly certain of the constants recorded by Thorpe. There was all the more reason for this, since Thorpe's material was not completely inactive optically but revealed a slight dextrorotation of 6.9' in a 200 mm. tube. Thorpe himself is inclined to attribute this deviation to the presence of a "trace" of "terpene;" "although not to a greater extent than 0.5 percent." For this reason a partial reëxamination of the constants was made by Roland E. Kremers in 1915. His material had been purified with fuming sulphuric acid and was totally inactive. However, no matter how carefully purified with sulphuric acid, potassium permanganate solution, and metallic sodium in the order recorded, the product had an odor that was regarded foreign to heptane.

Since then the preliminary work on the chemistry of the heptane solution has suggested several new methods for the purification of the heptane already largely purified by fractional distillation. In order to try out these methods, the fractions obtained by steam distillation of the oil of Jeffrey pine were refractionated with a short column and fraction 96–97° thus obtained was purified with the aid of one of the following chemicals:

1. Iodine.
2. Hydrogen iodide.
3. Hydrogen chloride.
4. Antimony trichloride.
5. Bromine and hydrogen bromide.

It seemed reasonable to expect that a comparison of the physical constants of heptane purified

- 1, by Thorpe with sulphuric and nitric acids,
- 2, by R. E. Kremers with sulphuric acid and permanganate solution, and
- 3, by the chemicals enumerated,

ought to admit of conclusions that might be as near the truth as we may reasonably hope to attain.

I. PURIFICATION OF HEPTANE.

Fractionation of Oil of *Pinus Jeffreyi*.

The material used in these experiments consisted of a ten-gallon lot of heptane, or "Abietene," purchased from Mr. D. F. Fryer of Santa Rosa, California.

It had been shipped in a 10-gallon galvanized iron can and was colorless, or at most slightly milky from what appeared to be suspended water. The odor was pleasantly aromatic and identical with that of *Pinus Jeffreyi* oil distilled in this laboratory from the oleoresin. There was no trace of empyreumatic odor.

First Fractionation.—The heptane was subjected to a preliminary fractionation. For this purpose the oil was divided into four approximately equal parts and each part fractionated in three large fractions as herewith recorded:

No.	1. Ce.	2. Ce.	3. Ce.	4. Ce.
Amount.....	9500	9500	9500	10200
First fr.....	1800	1900	2000	2000
Second fr.....	5600	5950	6000	6000
Third fr.....	1800	1500	1350	2000
Recovered.....	9200	9350	9350	10000
Loss.....	300	150	150	200

The above figures, which are roughly quantitative, reveal a loss of approximately 2 percent. This was due, partly to a defect in the apparatus, partly to a resinous residue left in the still.

Second Fractionation.—The corresponding fractions of each of the four distillations were united and again fractionated serially with steam. This time the distillate was collected in fractions of approximately one liter. After the bulk of the first fraction had been driven over, the middle fraction was added to the residue in the still, and so in turn the third portion. In all 36 liter fractions were obtained; liter fractions 1 to 6, inclusive, were obtained from the first large fraction; liter fractions 7 to 25, inclusive, from the middle portion; and liter fractions 26 to 36, inclusive, from the last portion. Fraction 37 was obtained by cohobating the total aqueous distillate obtained in the fractionation with steam.

The density of the oils was determined at 22° C. by means of a Mohr-Westphal balance. Strict accuracy was attained only to three places. The results are tabulated herewith:

Fraction.	Density 22°.	Fraction.	Density 22°.
1.....	0.682	19.....	0.683
2.....	0.682	20.....	0.683
3.....	0.682	21.....	0.683
4.....	0.682	22.....	0.683
5.....	0.682	23.....	0.683
6.....	0.682	24.....	0.683
7.....	0.682	25.....	0.683
8.....	0.682	26.....	0.685
9.....	0.682	27.....	0.686
10.....	0.682	28.....	0.687
11.....	0.682	29.....	0.687
12.....	0.682	30.....	0.688
13.....	0.682	31.....	0.691
14.....	0.683	32.....	0.693
15.....	0.683	33.....	0.710
16.....	0.683	34.....	0.739
17.....	0.683	35.....	0.836
18.....	0.683	36.....	0.858
		37.....

The densities here recorded clearly reveal that most of the liter fractions are relatively pure heptane, the density of which, according to Thorpe, is 0.6885 at about 15°, and, according to R. E. Kremers, is 0.6828 at 20°. On the whole, the density is slightly lower than that of the corresponding liter fractions from the oil of *Pinus Sabiniana* obtained by the same operator in 1915.¹ This is possibly due to the fact that the liter fractions in this case represent a second fractionation.

Third Fractionation.—In order to obtain a better insight into the character of the fractions than the densities afforded, three of them, *viz.*, liters 1, 25 and 34, were refractionated.

Liter No. 1.—500 Cc. were fractionated with the aid of a two-bulb fractionating column, an electric hot plate being used to heat. The following fractions were collected and their densities determined:

Fraction.	Boiling point.	Volume. Cc.	Density 24°.
1.....	-94° C.	a few Cc.
2.....	94-96	156	0.680
3.....	96-97	208	0.681
4.....	97-100	88	0.680
5.....	Residue	45	0.689
		—	
		497	

No positive tests for aldehydes by Schiff's reagent were obtained. The fractions were neutral to litmus. The balance of the first liter was distilled in like manner. It is apparent that even the first liter contains but little material boiling below the boiling point of heptane.

Liter No. 25.—The liter was distilled in two portions as follows:

Fraction.	Boiling point.	Volume. Cc.	Density 23°.
1.....	-96° C.
2.....	96-97	405	0.680
3.....	97-100	75	0.682
Residue.....	above 100
		—	
		480	
Fraction.	Boiling point.	Volume. Cc.	Density 24°.
1.....	-96° C.
2.....	96-97	440	0.681
3.....	97-100	85	0.683
4.....	above 100
		—	
		525	

The above data show that this liter consists principally of heptane and but little of any higher boiling substances.

Liter 34.—This liter yielded, as was to be expected, somewhat different results. The results of the first half are herewith recorded:

Fraction.	Boiling point, ° C.	Volume. Cc.	Density.
1.....	100-112	262	d ₂₅ 0.688
2.....	112-130	70	d ₂₅ 0.710
3.....	130-150	36	d ₂₅ 0.753
4.....	150-168	122	d ₂₅ 0.834
5.....	residue	20	d ₁₅ 0.842
		—	
Total.....		510	

In order to obtain a more correct interpretation of the character of these fractions, the above series was refractionated with the following results:

Fraction.	Boiling point. ° C.	Volume. Cc.	Density.	α_D . Degrees
1.....	-100	212	d_{25} 0.681
2.....	100-115	108	d_{20} 0.688
3.....	115-145	7
4.....	145-160	45	d_{15} 0.816	-12
5.....	160-168	90	d_{15} 0.850	-14
6.....	residue	40	d_{15} 0.887	-12

The higher fractions absorbed bromine violently. Not very much gas was given off by the addition of sodium. Hence it becomes apparent that one of the highest liter fractions contained traces of terpenes. The second half of fraction 34 was distilled in like manner. As before, the first fractionation gave a large fraction 100-115°; a smaller one 115-145°. Refractionated, the final fractions are as follows:

No.	Boiling point. ° C.	Volume. Cc.
1.....	96-100	225
2.....	100-115	96
3.....	115-145	20
4.....	residue	200
		540

With the above data as a means of interpreting, in a general way, the character of the liter fractions, all of them were refractionated. Up to liter 12 inclusive no special record was kept. After that it seemed worth while to record the results of the fractionations. As a rule, two of the liter fraction bottles were fractionated in three portions. For the most part the two liter fractions resolved themselves into the four fractions tabulated herewith. In each fractionation the temperature was raised to 115°. At the end the residue in the still boiling above 115° was fractionated and recorded at the bottom of the first column.

TEMPERATURE RANGE.

Lit.	Amt. used. Cc.	-96°. Cc.	96-97°. Cc.	97-100°. Cc.	100-115°. Cc.	Amt. recd. Cc.
13 and 14.....	700	4	610	65	0	679
	700	55	600	86	11	752
	718	10	585	107	10	712
15 and 16.....	700	0	584	101	16	701
	700	5	570	112	6	698
	690	0	560	117	10 sl. loss	687
17 and 18.....	700	10	568	113	10	701
	700	6	578	95	20	699
	790	0	665	104	18	787
19 and 20.....	700	0	535	140	20	695
	700	0	510	160	18	688
	730	17	565	123	25	730
21 and 22.....	700	5	542	120	26	693
	700	32	523	110	25	690
	750	0	605	120	30	755

Lit.	Amt. used. Cc.	-96°. Cc.	96-97°. Cc.	97-100° Cc.	100-115°. Cc.	Amt. recd. Cc.
23 and 24.....	700	6	525	138	30	698
	700	38	486	127	37	688
	730	10	525	144	45	724
25 and 26.....	700	5	410	208	70	693
	700	5	280	350	105	750
	800	2	90	585	105	782
27 and 28.....	700	..	10	500	165	675
	700	5	5	480	207	697
	730	490	220	710
29 and 30.....	700	370	270	640
	700	365	310	675
	712	..	10	335	355	700
31 and 32.....	700	195	470	665
	700	145	492	637
	610	25	515	...

115-145°—85 Cc.

145-(200)°—120 Cc. The temperature stood at 162° for the major portion.

CHEMICAL PURIFICATION OF HEPTANE FRACTION.

The well-established method of purifying hydrocarbon mixtures of the paraffin series consists of the treatment with sulphuric acid or with a mixture of sulphuric and nitric acids. This is the method employed by Thorpe.² It was originally supposed that these hydrocarbons were not acted upon by these reagents that proved so successful in attacking hydrocarbons of the benzene series; hence the designation paraffins. However, it was shown by Worstall³ that these hydrocarbons are not altogether indifferent to the action of these reagents in their concentrated form. Hence, while the treatment with fuming sulphuric acid may serve a very useful purpose, even in quantitative work when applied to the assay of petroleum hydrocarbons in turpentine oil, it does not follow that the product thus treated is sufficiently pure for the most exact determination of physical constants. That the heptane from Digger's pine oil, treated with concentrated sulphuric and nitric acids by Thorpe, was not even altogether free from terpenes is revealed by the slight optical activity of his purified hydrocarbon and is candidly admitted by this careful investigator. Gruse,⁴ who purified heptane with which a large amount of terpenes had been admixed, used fuming sulphuric acid and thus obtained a product that was optically inactive in a 200 mm. tube. Heptane from Jeffrey pine purified with sulphuric acid and subsequently treated with permanganate and metallic sodium by R. E. Kremers¹ was likewise inactive. Digger's pine heptane had previously been treated in like manner by Wm. Rabak.¹ These highly purified products, however, had a distinct spicy odor apparently not due to heptane. Whether the substance or substances to which this odor is due are formed by the sulphuric acid employed or by the subsequent treatment with permanganate is of little consequence. So long as their presence is perceptible, attempts to purify heptane by reagents that would either not form them or at least remove them seemed desirable. The opportunity to obtain a hydrocarbon of the methane series in a high degree of purity seemed too good to be ignored.

The preliminary survey of the chemistry of the heptane solution made during the academic year 1916-17 had suggested at least these methods of purification, viz.:

1. With iodine.
2. With hydrogen iodide.
3. With hydrogen chloride.
4. With antimony trichloride.
5. With bromine and hydrogen bromide.

These were tried out with liter quantities of fraction 96–97° as described below.

1. *Purification with Iodine.*—10 Gm. of powdered iodine were shaken with a liter of heptane and exposed to the sun until the deposition on the inside of the bottle prevented the penetration of light. The solution was filtered into another bottle and again exposed to sunlight. This operation was repeated until no further deposit was formed. The final filtrate was shaken with metallic mercury to remove the iodine and the heptane again filtered. To this filtrate a considerable quantity of sodium was added and the contents of the bottle shaken repeatedly for a week. The sodium was but slightly attacked.

The heptane thus purified was fractionated in two approximately equal portions, the distillate in each case being collected in 50 Cc. fractions with the results herewith tabulated:

Fractions. No.	Total distillate.	Fractionation.	
		I. Degrees.	II. Degrees.
1.....	1st drop	96.2	95.9
	5 Cc.	96.70	96.55
	10 Cc.	96.90	96.70
	25 Cc.	97.10	96.89
	50 Cc.	97.16	96.97
2.....	100 Cc.	97.22	97.02
3.....	150 Cc.	97.27	97.07
4.....	200 Cc.	97.29	97.16
5.....	250 Cc.	97.31	97.18
6.....	300 Cc.	97.34	97.19
7.....	350 Cc.	97.38	97.26
8.....	400 Cc.	97.40	97.30
9.....	450 Cc.	97.43	97.31
10.....	500 Cc.	97.46	97.54
	520 Cc.	98.60
11.....	550 Cc.	97.61
12.....	571 Cc.	98.05

Fraction 12 of the first fractionation revealed traces of iodine. In both fractionations fractions 2 to 10, inclusive, came over within a few tenths of a degree, thus revealing a remarkable degree of purity for so large an amount as 450 Cc. in each case. Hence these fractions were bulked and considered as a unit.

2. *Purification with Hydrogen Iodide.*—As a means of purification and to obtain a solution for preliminary work, heptane was saturated with hydrogen iodide gas generated in the usual way from iodine and phosphorus. Because of vapors carried over and decomposition, iodine became mixed with the solution. This iodine—hydrogen iodide solution remained for several weeks during which time portions were used for other experimental work, but no such recovered heptane was returned to this portion and is not represented here. After washing with alkali and drying over sodium, fractionation with a column and collection of the distillate in equal fractions gave the following table:

No.	I.		II.	
	Total distillate.	T. Degrees.	Total distillate.	T. Degrees.
1.....	1st drop	95.90	1st drop	95.7
	25 Cc.	96.70	25 Cc.	96.73
	50 Cc.	96.82
2.....	75 Cc.	96.80	100 Cc.	96.91
3.....	125 Cc.	96.87	150 Cc.	96.98
4.....	175 Cc.	96.90	200 Cc.	97.00
5.....	225 Cc.	96.93	250 Cc.	97.02
6.....	275 Cc.	96.98	300 Cc.	97.02
7.....	325 Cc.	97.00	350 Cc.	97.08
8.....	375 Cc.	97.04	400 Cc.	97.11
9.....	425 Cc.	97.06	450 Cc.	97.13
10.....	475 Cc.	97.09	500 Cc.	97.16
11.....	525 Cc.	97.10	550 Cc.	97.20
12.....	575 Cc.	97.11	600 Cc.	97.30
13.....	625 Cc.	97.20	650 Cc.	97.70
14.....	675 Cc.	97.32	700 Cc.	100.8
15.....	725 Cc.	98.10
16.....	747 Cc.	100.5

Fractions 3 and 4 of I were redistilled as part of II. At the end of Series I iodine appeared in the distillate. The residue had a blue color which appeared in the residual liquid also. Slight overheating of this residue in the sand bath gave a white color. The flask distilled entirely dry.

In Series I fractions 5 to 13, inclusive, were mixed, and in Series II fractions 2 to 11, inclusive, were mixed and the entire amount distilled rather more slowly on the intermediate heat with the flask and part of the projecting thermometer surrounded closely by asbestos paper. This gave 900 Cc. with a boiling range of 0.30°. The condenser was steamed out with heptane vapor before this run.

No.	Total distillate.	Fractionation.	
		I. Degrees.	II. Degrees.
1.....	1st drop	96.05	96.25
	10 Cc.	96.54	96.70
	25 Cc.	96.68	96.80
	50 Cc.	96.77	96.90
2.....	100 Cc.	96.82	96.91
3.....	150 Cc.	96.87	96.98
4.....	200 Cc.	96.89	97.00
5.....	250 Cc.	96.89	97.02
6.....	300 Cc.	96.85	97.03
7.....	350 Cc.	96.89	97.06
8.....	400 Cc.	96.90	97.09
9.....	450 Cc.	96.95	97.10
10.....	500 Cc.	97.01	97.13
	535 Cc.	97.20
11.....	550 Cc.	97.32
	585 Cc.	98.70
12.....	590 Cc.	100.
	615 Cc.	98.80
13.....	635 Cc.	101.7

In Series I, fractions 4 to 10, inclusive, were combined and in Series II, fractions 3 to 10, inclusive. These portions came over within 0.23°, respectively. The hot flask showed no liquid residue, only a few slight rings of discoloration.

3. *Purification with Hydrogen Chloride.*—Dry hydrogen chloride was passed into the heptane kept cold by means of ice water. The stopper of the bottle having been tied down, the saturated solution was allowed to stand for a week or more. The heptane solution was then poured off the resinous deposit which had been formed; washed with water and dried with sodium wire. As in the previous experiment, the heptane thus purified was subjected to fractionation in approximately equal portions and the distillate collected in 50 Cc. fractions as herewith recorded:

No.	Total distillate.	Fractionation.	
		I. Degrees.	II. Degrees.
1.....	1st drop	95.80	95.50
	5 Cc.	96.30	96.30
	10 Cc.	96.48	96.45
	25 Cc.	96.66	96.68
	50 Cc.	96.76	96.80
2.....	100 Cc.	96.82	96.90
3.....	150 Cc.	96.90	96.92
4.....	200 Cc.	96.91	96.95
5.....	250 Cc.	96.94	96.98
6.....	300 Cc.	96.99	97.00
7.....	350 Cc.	97.01	97.02
8.....	400 Cc.	97.05	97.10
9.....	450 Cc.	97.09	97.30
10.....	500 Cc.	97.30	98.30
11.....	550 Cc.	100.90	517 Cc. 101.70

Fractions 2 to 9, inclusive, of both series came over within 0.3° and 0.4° , respectively. Although the range of boiling temperature for each 400 Cc. is less than one-half degree, it is not quite as narrow as that of the heptane purified by means of iodine.

A second lot of heptane was saturated with dry hydrogen chloride for the purpose of solubility and other experimental work. This stood from December 3 to January 24. What remained was washed with water and dried over sodium for days and finally distilled over a little sodium and the best fractions combined.

No.	Total Distillate.	I.	II.	III.
		Distilled 1/24. Degrees.	Distilled 1/25. Degrees.	Distilled 1/25. Degrees.
1.....	1st drop	95.60	95.60	95.80
	25 Cc.	96.42	96.54
	50 Cc.	96.25	96.51	96.60
2.....	100 Cc.	96.34	96.59	96.70
3.....	150 Cc.	96.40	96.65	96.72
4.....	200 Cc.	96.44	96.69	96.78
5.....	250 Cc.	96.49	96.71	96.80
6.....	300 Cc.	96.52	96.74	96.84
7.....	350 Cc.	96.57	96.80	96.90
8.....	400 Cc.	96.59	96.80	96.90
9.....	450 Cc.	96.60	96.83	97.00
10.....	500 Cc.	96.63	96.90	97.20
11.....	550 Cc.	96.70	96.94	98.25
12.....	600 Cc.	97.00	97.01
	620 Cc.	101.50
13.....	650 Cc.	98.60	97.00
14.....	101.90 (dry)

In Series I fractions 3 to 10, inclusive, in Series II fractions 3 to 11, inclusive, and in Series III fractions 3 to 9, inclusive, were all combined and refractionated. The temperature range in the three series was 0.36° , 0.42° and 0.40° giving, respectively, 450 Cc., 500 Cc., and 400 Cc. of distillate.

No.	Total distillate.	Fractionation.	
		I. Degrees.	II. Degrees.
1.....	1st drop	95.70	96.60
	10 Cc.	96.87	97.00
	25 Cc.	97.10	97.20
	50 Cc.	97.20	97.22
2.....	100 Cc.	97.25	97.29
3.....	150 Cc.	97.30	97.30
4.....	200 Cc.	97.30	97.32
5.....	250 Cc.	97.30	97.38
6.....	300 Cc.	97.32	97.39
7.....	350 Cc.	97.37	97.40
8.....	400 Cc.	97.38	97.40
9.....	450 Cc.	97.40	97.50
10.....	500 Cc.	97.40	97.65
	525 Cc.	97.85
11.....	550 Cc.	97.40
	585 Cc.	100.90
12.....	600 Cc.	97.40
13.....	650 Cc.	97.40
14.....	700 Cc.	97.44
15.....	750 Cc.	97.52
16.....	800 Cc.	98.70

The flask contained no residue except a stain on the walls, the odor of which was slightly resinous. The last fractions of the distillate had an odor of kerosene.

For the purpose of still more accurate boiling-point determinations and ascertaining the values of the other physical constants in Series I, fractions 3 to 14, inclusive, and in Series II, fractions 3 to 9, inclusive, were combined, giving temperature ranges of 0.19° and 0.21° and distillates of 550 and 300 Cc., respectively.

4. *Purification with Antimony Trichloride.*—For this purpose a liter of heptane was shaken repeatedly with 15 Gm. of antimony chloride for a period of more than eight days. A reddish, sticky deposit was formed on the crystals of antimony chloride and was given off to the walls of the bottle during shaking so that fresh surfaces of the antimony chloride were exposed to the slight impurities in the heptane. In order to remove the antimony chloride in solution, the heptane was shaken with water; the mixture filtered; the heptane dried with sodium wire, and finally fractionated as in the earlier purification.

No.	Total distillate.	Fractionation.	
		I. Degrees.	II. Degrees.
1.....	1st drop	95.50	95.40
	5 Cc.	96.25	96.30
	10 Cc.	96.45	96.45
	25 Cc.	96.65	96.65
	50 Cc.	96.78	96.80
2.....	100 Cc.	96.84	96.89
3.....	150 Cc.	96.89	96.91
4.....	200 Cc.	96.91	96.93
5.....	250 Cc.	96.94	96.97

6.....	300 Cc.	96.97	96.99
7.....	350 Cc.	97.00	97.00
8.....	400 Cc.	97.02	97.06
9.....	450 Cc.	97.07	97.27
10.....	500 Cc.	97.24	100.50
11.....	550 Cc.	98.75

Again the bulk of the heptane, *viz.*, fractions 2 to 9, inclusive, distilled over within narrow limits, namely 0.3°.

5. *Purification with Bromine and Hydrogen Bromide.*—That portion of heptane recovered from the action of bromine and also that which had been treated with hydrogen bromide, was combined and washed with water and dilute alkali and allowed to stand over calcium chloride. This was fractionated allowing the high boiling residue to remain in the flask until the entire quantity had been fractionated.

No.	Total distillate.	Fractionation.		
		I. Degrees.	II. Degrees.	III. Degrees.
1.....	1st drop	95.90	97.10	98.00
	10 Cc.	97.15	97.50
	25 Cc.	97.45	97.85	98.35
	50 Cc.	97.60	98.20	98.50
2.....	100 Cc.	97.80	98.40	98.70
3.....	150 Cc.	98.00	98.55	98.85
4.....	200 Cc.	98.10	98.72	98.90
5.....	250 Cc.	98.20	98.95	99.00
6.....	300 Cc.	98.45	99.20	99.20
7.....	350 Cc.	98.65	99.50	99.40
8.....	400 Cc.	98.90	99.90	99.70
9.....	450 Cc.	99.20	100.50
10.....	500 Cc.	99.90	101.35
11.....	550 Cc.	100.65	102.40	100.70
12.....	600 Cc.	102.15	105.00	101.40
13.....	650 Cc.	102.20
14.....	700 Cc.	103.40
15.....	750 Cc.	104.00
16.....	800 Cc.	105.50
17.....	830 Cc.
18.....	876 Cc.	160-205

The fractions obtained by this distillation were treated for five days with sodium wire. This removed the remaining moisture and perhaps some bromine derivative. The remaining heptane was again fractionated and collected within narrower limits of temperature.

No.	Total distillate.	Fractionation.			
		I. Degrees.	II. Degrees.	III. Degrees.	IV. Degrees.
1.....	1st drop	95.90	96.40	96.00	96.40
	10 Cc.	96.40
	25 Cc.	96.60	96.80	96.80
	50 Cc.	96.72	96.88	97.00
.....	70 Cc.	97.03
	100 Cc.	96.83	97.12	97.20	97.20
3.....	150 Cc.	96.89	97.25	97.31	97.36
4.....	200 Cc.	96.92	97.32	97.40	97.44
5.....	250 Cc.	96.98	97.40	97.47	97.50
6.....	300 Cc.	97.04	97.47	97.56	97.60

No.	Total distillate.	Fractionation.			
		I. Degrees.	II. Degrees.	III. Degrees.	IV. Degrees.
7.....	350 Cc.	97.13	97.60	97.70	97.70
8.....	400 Cc.	97.20	97.75	97.83	97.80
9.....	450 Cc.	97.30	97.90	98.00	97.94
10.....	500 Cc.	97.42	98.10	98.20	98.02
11.....	550 Cc.	97.62	98.32	98.55	98.30
12.....	600 Cc.	97.90	98.85	99.40
13.....	650 Cc.	99.00	99.00	100.50
	670 Cc.	103.80
14.....	700 Cc.	101.90	102.90
15.....	720 Cc.	102.40
	740 Cc.	104.00

This product was not of the high degree of purity of the preceding fractionations because it was mixed with bromine substitution products which were not entirely removed by the two treatments with sodium and fractionation. The distillate had a sweet odor resembling the lower alkyl halides and entirely different from that of the heptane purified by the other methods. Those fractions within one degree were combined and this sample then reserved for photo-experiments. Further determinations of physical constants were made more for the sake of comparison than in the hope that it would have the high degree of purity of the other samples.

(Continued in December Number.)

* Editor's Note:—The bibliography, references to which are made in this part, will be printed at the conclusion of this contribution, December issue.

PLANT ASSOCIATIONS.*

BY HEBER W. YOUNGKEN.

Alike with humans and other animals, plants have developed, during the ages, definite habitat relations with their surroundings.

If we look about in nature we invariably find certain definite species of plants growing in the same locality, in the same kind of soil and subject to the same climatic conditions as other species with which they are associated. Thus, we are accustomed to find American hellebore growing in moist low areas of woodlands or meadows alongside of skunk cabbage; sphagnum, with drosera; the pitcher plants, cranberries and bladderworts in bogs; scrub oaks, beeches, maples, sour gums, bracken, holly, etc., in pine barrens; the splatterdocks, pondweeds, water-lilies and water-hyacinths in ponds; cacti and century plants in sandy, hot, desert regions. In each of these instances we recognize a distinct group of plants. This, then, in its entirety, occurring in a common locality, is what is recognized as a plant association.

Plant associations have been grouped in a number of ways depending either upon the relation they have assumed to various factors of environment such as light, temperature, water, other plants and animals or upon the principle of succession. There are advantages to be had in each method of grouping. In this brief exposition, however, they will be classified solely on the basis of their relation to water.

* Read before Scientific Section, A. Ph. A., City of Washington meeting, 1920.