

THE SEPARATION AND IDENTIFICATION OF HYDROCARBONS
IN A DISTILLATE OBTAINED DURING THE
MANUFACTURE OF CORK BOARD

BY

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INTRODUCTION

For many years, the chemical constitution of cork has been studied, most investigators having started their researches with the ground cork of commerce. Zetzsche²⁶ reviewed the literature on this subject and gave the results of his own investigations. According to Zetzsche, the constituents of cork may be divided into five fractions:

1. Substances extracted by boiling water.
2. Substances which dissolve in fat solvents such as chloroform and alcohol. This fraction contained cerin and friedelin, which Zetzsche referred to as the wax alcohols, and also fats and free fatty acids.
3. Compounds which go into solution by treatment with dilute sodium hydroxide and sodium sulfite. These include cork lignin, a part of the tannins, and nitrogen containing substances.
4. Substances which go into solution when the residue from the above treatment is saponified with alcoholic alkali. These are high molecular weight fatty acids, of which three have been recognized: phellonic acid, melting point 96° ; phloionic acid, melting point $120-121^{\circ}$; and suberic acid. The melting point of the latter was not given.
5. The tannins, cellulose, and cellulose-similar products remain insoluble in the alkali. Additional ingredients

of the residue are nitrogen containing compounds, which are probably albumins, colored substances, and inorganic compounds.

Zetzsche²⁷ gave for the empirical formulae of phellonic, phloionic, and phloionolic acids $C_{22}H_{44}O_3$, $C_{18}H_{34}O_6$, and $C_{18}H_{36}O_5$ respectively. Carhart² later proved by degradation and synthesis that phellonic acid is twenty two hydroxy tetracosanic acid.

In recent years a series of investigations at the University of Maryland have shown that cerin and friedelin are triterpenoids, the former being a hydroxy ketone and the latter a ketone⁹. The amorphous material left in the ethyl acetate extract of cork after cerin and friedelin have precipitated has been shown to contain small quantities of a sterol^{6, 14}.

When cork bark is treated with high pressure steam, a sticky, foul-smelling, brown tar steam distills out. The cork that is left is pressed and used as insulating board. It was the purpose of this investigation to identify some of the substances present in the steam distillate.

SECTION I

HISTORICAL

A. Separation and identification of hydrocarbons from natural sources.

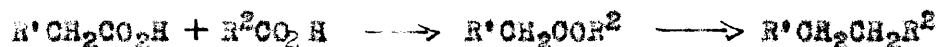
Krafft¹⁷ in 1907 fractionated the higher normal paraffins of lignite by distillation, using the very high vacuum of "the cathode light". By refractionating a number of times, he claimed to have obtained every straight chain homolog from nonadecane to hexatriacontane. His identification was based on the boiling points, melting points, and specific gravities of the hydrocarbons when just liquid, as compared with these constant for synthetic compounds.

Glud¹² obtained from coal paraffin what he considered to be pure straight chain hydrocarbons containing from twenty-four to twenty-nine carbon atoms. The heptacosane was obtained by crystallization from acetone, while the others were obtained by repeated fractional distillation of the crude paraffins. Glud based his identification on a comparison of melting points, boiling points, and refractive indices with those of synthetic compounds under the same conditions.

Buchler and Graves¹ recrystallized petroleum wax from ethylene dichloride until the melting point and refractive index were constant. Distillation gave a series of fractions, the average molecular weight of which they determined cryoscopically, using dichlorobenzene as solvent. They also determined the density and refractive index of each fraction. The molecular refractions obtained agreed well with those calculated, assuming the atomic refraction of carbon was 2.501 and hydrogen 1.051. Though the melting points and molecular weights of their purified

fractions were in close agreement with the Krafft^{15, 16} synthetic hydrocarbons, the authors stated they were not individual homologs but mixtures.

Channon and Chibnall³ in 1929 reported the presence of nonacosane in large quantities in the ether-soluble part of cabbage leaves. A comparison of melting point, set-point, and crystal spacing with the constants for the synthetic hydrocarbon indicated they had isolated pure nonacosane. The large number of orders of reflection obtained in their x-ray diffraction pattern also was a sign of purity. From cabbage leaves these investigators also obtained 15-nonacosanone. This suggested the following mechanism of wax metabolism in the plant:



Chibnall and Piper⁴ showed that the transition points which hydrocarbons gave on heating and cooling were reliable indices of the degree of purity of a mixture of paraffins, while melting points and long crystal spacings were chiefly of value as measures of the mean molecular weights. The transition points apparently involved structural changes. The crystalline form at room temperature went over to a colorless glassy form when the first transition point was reached, and this in turn changed at the second transition point to another crystalline form. The three forms of the hydrocarbons existing at different temperatures were the so-called A, B, and C forms, which differed in the angle of tilt of the long dimension of the unit cell to the short side. The A form, which was the normal state for odd numbered hydrocarbons, had the long axis practically vertical. The first transition point on heating which is the one referred to hereafter in this thesis whenever transition point is mentioned, unless another is specifically described, was very sensitive to impurities. Since the transition point curve for

mixtures of two paraffins had a minimum (see fig.15, page 45), the transition point of any mixture was not the same as that of a pure hydrocarbon of the same mean molecular weight, but somewhat lower. Chibnall and Piper made a comprehensive study of the transition points, melting points, set-points, and long crystal spacings of a series of known pure hydrocarbons and known mixtures. On the basis of their work, they made a number of generalizations, and made a series of suggestions to aid in the separation of hydrocarbons from mixtures.

Firstly, they stated an experienced eye could tell from a glance at an x-ray photograph whether a sample was approaching purity. As mixtures approached equimolar proportions, only a few orders of reflection appeared, these however standing out more sharply than in plates of more nearly pure materials. A pure paraffin generally gave eight or more orders. The melting points of equimolar mixtures of two or three paraffins were sharp and corresponded to the mean molecular weights. Thus an equimolar mixture of hexacosane and octacosane melted at the same temperature as heptacosane, since melting point versus composition gave a perfectly straight line. The melting points of equimolar mixtures of four or more paraffins were indistinct, but were in the region corresponding to the mean molecular weights.

For equimolar mixtures of three or four paraffins, the transition points were very indistinct and occurred at that of the lowest member in the mixture. Equimolar mixtures of five paraffins gave no transition points at all. With equimolar mixtures of two paraffins separated by three or more carbon atoms, the transition points were not well-defined, but the second transition points on heating were very marked, and occurred a degree to a degree and a half below the melting

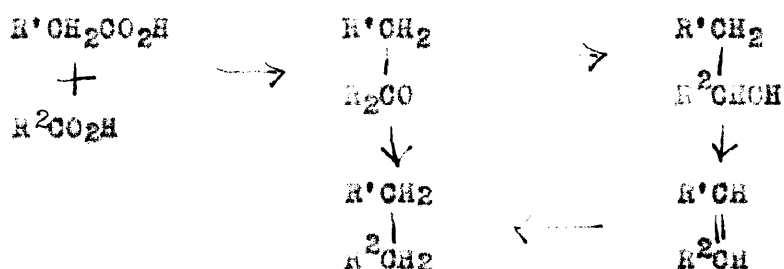
points instead of the three tenths to five tenths of a degree for pure compounds. Chibnall found that equimolar mixtures of two or three paraffins whose carbon contents did not differ by more than two or three, had sharp set-points which were not appreciably depressed below the set-points for pure paraffins with molecular weights the same as the average values for the mixtures. On slow cooling below the melting points, there was little tendency to supercool, the paraffin mixtures setting crystalline about a half degree below the melting points, just as for pure paraffins. Equimolar mixtures of more than three paraffins did not set crystalline.

The authors stated that in biochemical investigations it was improbable that pure paraffins would often be encountered, and that the isolation of paraffins of a recognizable degree of purity was always laborious and often impossible. However, by comparing physical constants, i. e. transition points, melting points, and spacings with the constants of known mixtures, the composition of simple mixtures could be estimated. In attempting the estimation of the composition of a mixture in which a maximum separation had been obtained by fractional crystallization, their procedure was first to measure the spacing, then pick out various binary mixtures having the same spacing. Then they selected that mixture whose melting point and transition point were in best accord with those of the unknown mixture. If the transition point was still too low by a degree or two, they arbitrarily estimated about five per cent of unknown impurity.

Chibnall⁵ separated the constituents of apple cuticle wax into primary alcohols, secondary alcohols, and paraffins. The primary alcohols were converted into the corresponding paraffins by means of phosphorus and hydriodic acid, and fractionally crystallized from light petroleum ether. A study of the melting points, transition points, and spacings

of the fractions obtained showed conclusively that the normal primary alcohols containing twenty-six, twenty-eight, and thirty carbon atoms were present in the original wax. Fractionation of the paraffin fraction of the wax showed the presence of heptacosane and nonacosane and the absence of any hexacosane or octacosane. The transition points of the various fractions were nearly all slightly lower than those of the suggested binary mixtures. That this was due to the presence of traces of the lower paraffin in the top fractions and of the higher paraffin in the lower fractions was verified by actually making several mixtures containing a small amount of the suggested impurity. Two to three per cent of added impurity was not sufficient to change the melting points or spacings appreciably, but the transition points were lowered as much as two to three degrees.

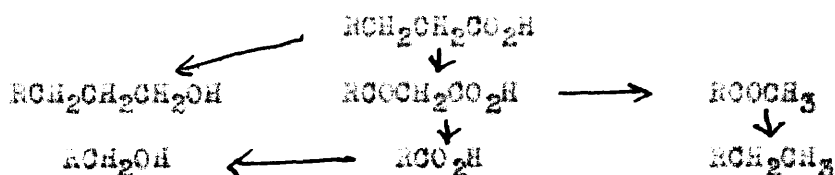
The secondary alcohol found in apple cuticle wax was D-10-nonacosanol. The presence of this alcohol along with nonacosane in the same wax suggested to Chibnall at that time the following mechanism for wax metabolism:



According to this mechanism, both the secondary alcohol and the hydrocarbon could be formed from the ketone. In Chibnall's research the ketone was not found, but later work on brussel sprouts leaf wax showed 15-nonacosanol, 15-nonacosanone, and nonacosane were all present. No olefins were found, however. In apple cuticle wax, this mechanism would postulate the presence of decanoic and eicosanoic acids.

Chibnall et al⁶ undertook a comprehensive investigation of the constitution of the primary alcohols, fatty acids, and paraffins in plant and insect waxes. They found that in two cases only had the samples of paraffins isolated from natural sources proved to be pure products, satisfying the requirements of x-ray analysis. In all cases examined they were mixtures, and separation by fractional crystallization was so laborious that in only one instance, apple cuticle wax, was it sufficiently complete to give a pure product. Analysis by means of the physical constants showed the presence of odd-numbered straight chain hydrocarbons, and no even-numbered homologs, in all samples examined. A number of the so-called even-numbered paraffins isolated from natural sources were examined and found to be mixtures of the odd-numbered hydrocarbons. Both the normal fatty acids and primary alcohols in all waxes studied contained only the homologs with an even number of carbon atoms.

Chibnall and Piper⁷ discussed the metabolism of plant and insect waxes. Since analysis of many wax products had shown they consisted almost exclusively of even-numbered straight chain primary alcohols and acids and odd-numbered paraffins, it was clear that paraffins were formed from the long chain acids present in waxes, not from the shorter glyceride acids as previously suggested. According to their hypothesis, long chain acids were initially formed by oxidation at the end of polymerized chains formed by condensation of sugar units. A series of acids like those in glycerides and waxes could then be obtained from these longer units by a process of beta oxidation. Reduction of any of these acids would give the corresponding even-numbered alcohol, while decarboxylation of the beta keto acid would give the (n-1) ketone. The ketone, in turn, was reduced to the hydrocarbon. The following is a diagram of Chibnall's latest mechanism for wax metabolism:



Markley et al²⁰ recently obtained by fractional crystallization of the unsaponifiable fraction of grapefruit peel wax a ketonic fraction and a hydrocarbon fraction. Persistent fractionation of the hydrocarbons resulted in mixtures with transition points depressed considerably, three to four degrees for the best fractions. They appeared, however, to contain principally nonacosane and hentriacontane, with possibly some lower and some higher members of the series present. X-ray spacings were used in interpreting the composition.

Markley, Sande, and Hendricks²¹ obtained from the hydrocarbon fraction of grape wax fractions which indicated the composition was about seventy per cent nonacosane and thirty per cent hentriacontane.

Gisvold and Rogers¹¹ in their book discussed the separation and identification of wax constituents.

B. Synthesis of straight chain hydrocarbons.

Krafft¹⁵ in 1882 prepared laurone by heating the barium salt of lauric acid at fifteen millimeters pressure with excess lime. He made the corresponding hydrocarbon by converting the ketone to the dichloride with phosphorus pentachloride and then reducing the dichloride with phosphorus and hydriodic acid. In this way he made the twenty-three and the thirty-five carbon homologs. In order to make the twenty-two carbon hydrocarbon, he used a mixture of barium palmitate and barium heptylate. Krafft¹⁶ prepared several paraffins by the action of sodium on the appropriate alkyl iodides.

hydrocarbons by first making the primary alcohols from the esters by means of the Bouveault-Blanc reaction, then converting the alcohols to the iodides, and treating the latter with zinc and hydrochloric acid. They also prepared tetracosane by treating the iodide in ether solution with magnesium:



Glud¹² obtained good yields of the ketone from the acid by heating the barium salt spread out on boiling chips in an evacuated combustion tube. The ketone was treated with phosphorus pentachloride and the dichloride treated with hydriodic acid to give the hydrocarbon in good yield. In this way, Glud made hexacosane, heptacosane, and octacosane.

Strating et al²⁴ made heneicosane and tricosane, using the Claisen condensation. In the synthesis of heneicosane, undecylenic acid was first hydrogenated to give the saturated acid. Esterification, treatment of the ester with sodium ethoxide, and saponification of the resulting product gave didecyl ketone, which was then reduced by the Clemmensen method to the hydrocarbon. Tricosane was made in a similar manner, starting with lauric acid.

SECTION II

EXPERIMENTAL

A. Separation and preliminary purification of the hydrocarbon mixture from the crude.

The material under investigation was obtained from the Crown, Cork, and Seal Company of Baltimore, Maryland. About 200 gms. of a brown waxy distillate from the crude had previously been obtained by another worker in this laboratory, who was looking for a good source of phellonic acid. He was unsuccessful in obtaining any quantity of acid from this material, and turned the distillate over to the present investigator. Great difficulty had been found in vacuum distilling the crude because of the large amount of water present. There was a great deal of foaming, and the distillation had to be watched very carefully. In this investigation it was found advisable to remove the water by distilling with xylene or benzene. The residual solvent came off readily when a vacuum and a small amount of heat were applied, and on raising the temperature the wax distilled without foaming. However, foul-smelling gases, probably sulfur or nitrogen containing compounds, were given off by the impurities present, and a high vacuum could not be maintained. Consequently the boiling point of the distillate went up to about $300^{\circ}/25$ mm.

Approximately 100 gms. of the crude was freed of water by mixing with 200 c.c. of xylene and distilling off the solvent. This process was repeated three times, using dry xylene. If a water trap was placed between a flask containing the crude plus the xylene and a reflux condenser, the water could be removed in about an hour with little attention.

The residual xylene adhering to the crude was removed by placing the mixture in a 500 c.c. sausage flask, turning on the vacuum, and heating gently. When the salt bath was raised to 335° and the pressure was 25 mm. (a water pump was used in the first distillation) the hydrocarbon started to distill. The boiling range was 230-250°, about 75 gms. of light yellow wax being obtained.

Ethyl alcohol was found to dissolve comparatively little of the wax, while removing much of the coloring matter. Alcohol was not satisfactory for recrystallization, however, since even when hot it dissolves only a small quantity of the wax. The distillate was found to crystallize well from acetone and also from propanol. Consequently, after extraction with ethanol, it was crystallized repeatedly from these two solvents until the melting point was constant. The product was pure white, and did not dissolve in concentrated sulfuric acid or dimethyl sulfate. It reacted neither with bromine in carbon tetrachloride nor potassium permanganate. The results of East camphor determinations of the molecular weight were not very satisfactory. Those obtained by the author indicated about twenty-nine carbon atoms in the chain, while those obtained by another analyst indicated only about twenty-one or twenty-two.

Solvent purification. 175 gms. of distillate was dissolved in 2.5 liters of hot acetone. On cooling 83 gms. of light-colored wax was obtained. On distilling the acetone from the filtrate, a brown wax was obtained. This wax was extracted with cold alcohol, then recrystallized once from acetone and once from propanol. The resulting product was combined with the first precipitate from acetone. The total yield was 39 gms. of material melting at 56°.

Analysis: Carbon 85.01, 84.85. Hydrogen: 13.07, 14.99.

Since it was evident that fractionation procedures would have to be used, a considerable quantity of the hydrocarbon mixture was purified. An attempt was made to purify the substance by chromatographing with alumina. The hydrocarbons were not adsorbed at all and a great deal of the impurities were removed. However, the process was slow and required a large amount of alumina to purify any quantity of hydrocarbons. Magnesium oxide and ten parts by weight of "HyFlo Super Cel", which is made by the Johns-Manville Company, also took the color out of a dilute benzene solution of the hydrocarbons. Neither of these chromatographic methods was thought suitable for the purification of large quantities of the crude wax. The procedure finally adopted was the extraction of a benzene solution of the hydrocarbons with cold concentrated sulfuric acid until addition of fresh acid no longer removed color from the solution. A total of about 300 gms. was thus purified. In the sulfuric acid-soluble fraction there was present a considerable quantity of dissolved solids which were thrown out by pouring into cold water. Repeated crystallization and charcoaling of the dark-colored material resulted in a small quantity of a light-colored solid which shrank in a capillary tube at 220° and melted at 239-240°. It was apparently a mixture of cerin and friedelin which had been carried over in the distillation, and nothing further was done with it. A cooling curve and carbon and hydrogen analyses indicated the mixture obtained by acid purification was about the same as that obtained by repeated crystallization of the crude wax.

Purification with sulfuric acid. 300 gms. of the waxy distillate was dissolved in benzene, and shaken with cold concentrated

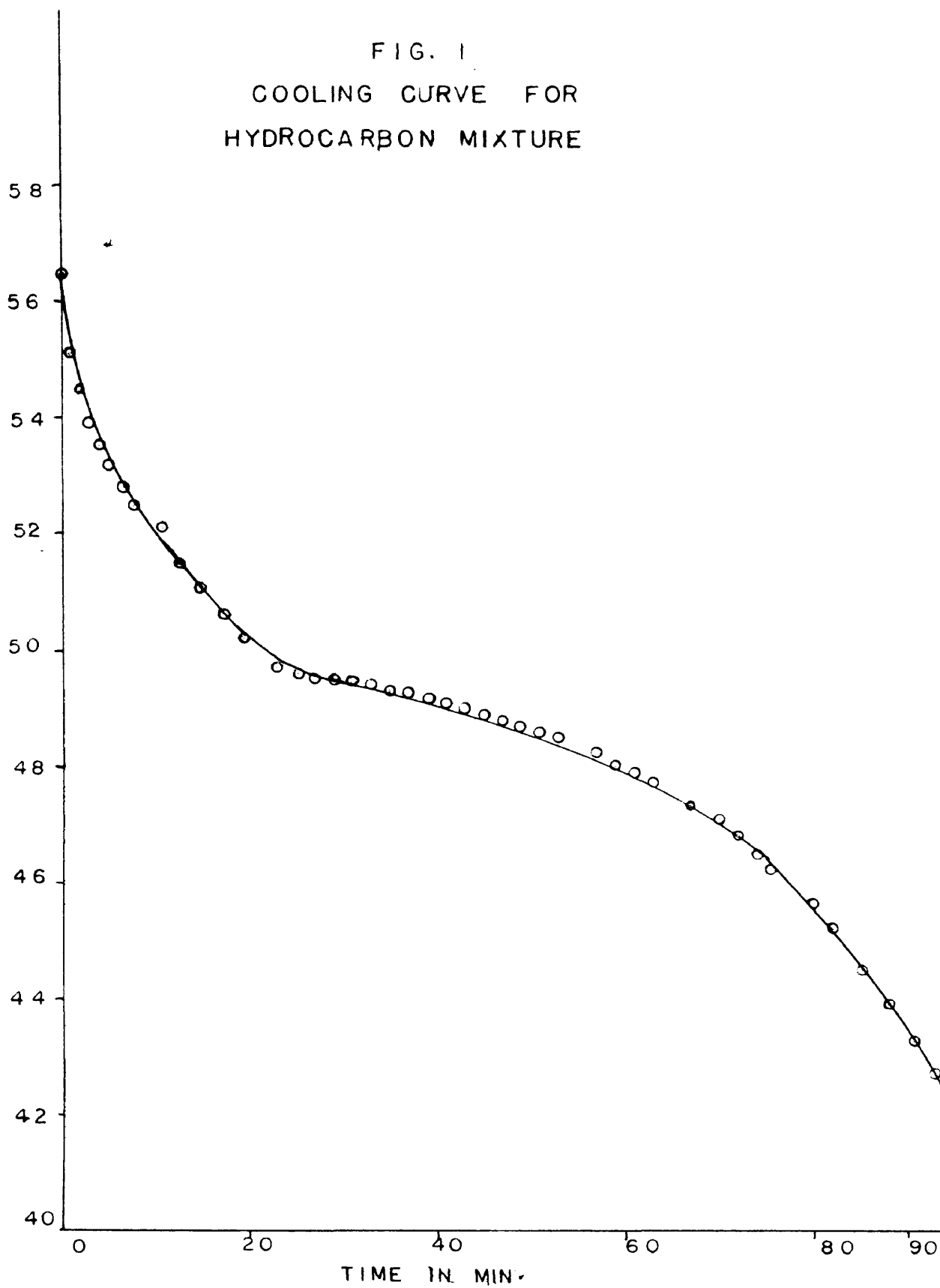
sulfuric acid in a separatory funnel. The acid colored considerably and fresh acid was added in small portions until it no longer became colored. The benzene solution was allowed to stand overnight with anhydrous sodium carbonate. A small amount of gelatinous material formed and the mixture was centrifuged. On removing the solvent by distillation on the steam bath, and then distilling the hydrocarbon mixture in vacuum, a white solid material was obtained. Two recrystallizations from acetone gave 125 gms. of product melting at 55°.

Cooling curve on the hydrocarbon mixture. The bath consisted of a battery jar of about ten liters capacity, placed in an ordinary enameled tub. Ground cork was placed below and around the jar in order to give slow cooling of the bath. Using a Variac, a constant rate of heating or cooling was easily obtainable. The sample of about 10 gms. was placed in an ordinary Pyrex test tube which was fitted with a short piece of large bore rubber tubing adjacent the lip. This served as a connecting piece between the smaller test tube and a larger one, creating a dead air space between the bath and the sample, to lag the heating or cooling effect of the bath on the sample. A spiraled metal stirrer was used and operated by hand. A Bureau of Standards calibrated 0-100° thermometer was placed in the middle of the melt. The initial temperature of the bath was 54° with the melt at 56.50. The bath was made to cool slowly at a controlled rate. The curve obtained is given in fig. 1, page 15.

B. Fractional distillation of the mixed hydrocarbons.

Slow fractional distillation at six millimeters pressure using a column about a foot and a half long, packed with glass helices and electrically heated, resulted in a series of fractions ranging from the

FIG. 1
COOLING CURVE FOR
HYDROCARBON MIXTURE



lowest, which consisted of material boiling up to 145° to the highest which boiled from 200-207°, as well as the usual brown still residue. Refractive indices of most of the fractions were obtained and comparison of these with Glaud's¹² values for pure hydrocarbons indicated roughly the mean number of carbon atoms. Thus, the average carbon content of the fraction boiling from 165-170° was about twenty-four, and increased steadily to about twenty-nine in the fraction boiling from 195-200°. The refractive indices of the highest and lowest boiling fractions were not determined. A summary of the results obtained by fractional distillation is given in the following table:

TABLE I

Boiling point in °C	Amount in gms.	Refractive index at 65°
Still residue	10.2	-----
200-207	13.1	-----
195-200	19.9	1.4367
186-195	19.2	1.4344
180-185	28.4	1.4339
180-200	5.5	-----
175-180	45.4	1.4323
165-175	42.9	1.4306
up to 155	44.4	1.4311
148-155	39.9	-----
up to 145	33.3	-----

The apparatus used consisted of a 3/4" column about 18" long

sealed to a 500 cc. flask and surrounded by an electrically heated air jacket. Two glass tubes were sealed to the flask, one for adding sample, the other to hold a boiling tube. No air was run into the flask from the outside, but the slow evolution of the air from the 5 mm. boiling tube was sufficient to prevent bumping. The column was packed with glass helices, the thermometer being attached by means of a piece of rubber tubing in the usual fashion. The arm conducting the distillate to the receiver was about a foot long and served as an air condenser. The receiver was a 200 c.c. distilling flask, the arm of which was connected to a manometer, which in turn was connected to a Cenco Hi-Vac pump. It was found necessary to surround the outlet tube with hot nichrome wire to prevent the paraffins from solidifying before they reached the receiver. It was convenient merely to extend the wire used in the jacket around the exit tube. To prevent flooding in the column it was necessary to keep the jacket temperature 20-30° above the distilling temperature. It was endeavored to have the liquid reflux about two thirds the length of the column. The rate of distillation was about a drop in three to four seconds with the bath temperature about 90° above the distilling temperature. 310 gms. of the paraffins was distilled, the whole apparatus being cooled each time a fraction was cut.

The indices were determined by using a Valentine refractometer #498, made by the Industro-Scientific Co., Phila., Pa. The temperature was kept at 65° by circulating through it water from a constant temperature bath. With the assembly used it was possible to hold the temperature constant to 0.1°.

C. Equilibrium melting of hydrocarbon fractions.

It was deemed advisable at this stage of the purification, to attempt further separation by means of equilibrium melting. This method was used by Hicks²⁵ and by Mair¹⁹ and was found very convenient and useful. Instead of using a vacuum-jacketed funnel as these investigators did, however, an apparatus was designed that allowed the material to be held at any desired temperature for a considerable length of time. The apparatus consisted of a special funnel attached to a side-armed Erlenmeyer flask, the whole being placed in a constant temperature bath. It was found more convenient to use the hydrocarbon mixture itself, rather than an ether or petroleum ether solution. It was only necessary to raise the temperature of the bath to any desired level, allow the contents of the funnel to come to equilibrium, and drain off the fractions into the attached Erlenmeyer flask.

Each of the fractions obtained by fractional distillation was cut into from three to five parts. On most of these small fractions the capillary melting points, set-points, and refractive indices were determined. It was noted that the melting points of the successive fractions increased as expected in regular fashion, but the refractive indices decreased. It was also noted that the higher fractions were lighter in color than the lower ones. The conclusion was obvious that impurities were present and were concentrating in the lower fractions. The presence of non-hydrocarbon impurities explained the unexpectedly large difference in the melting points of the highest and lowest cuts from each boiling fraction.

To get rid of the impurities, chromatographing with Brockman alumina was first tried. This raised the melting point somewhat, but the

hydrocarbons obtained still colored warm sulfuric acid. Since it was found that other investigators⁴ had purified solid hydrocarbons by treating them with concentrated sulfuric acid at 120° until fresh acid no longer was colored, each of the fractions obtained from the equilibrium melting was treated with sulfuric acid at 120-130°, the mixture being stirred by an electrical stirrer. One three hour treatment in this manner removed practically all of the materials that colored hot sulfuric acid. The melting points were raised considerably, fraction eight, for instance, changing from 49-50° to 51.8°. In Table II the melting points and set-points given are for the fractions after the acid treatment.

About a third of the total weight of hydrocarbons was lost by the acid treatment, part of the loss being due to the solubility of the hydrocarbons themselves in the acid, partly to mechanical losses, partly to the reaction with the oxygen-containing or unsaturated substances present.

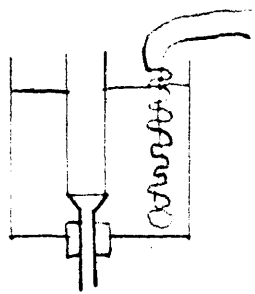
The first apparatus (Fig. 2a) used consisted of a large test tube 190X25 mm. with a short piece of 5 mm. tubing sealed on to the bottom. This was inserted in a rubber stopper and attached to an inverted five pound ether can with the bottom off, which made a convenient water bath. A copper coil in this bath through which water circulated, after having been run through an ice bath by means of a circulating pump, gave fairly constant low temperatures. Ether solutions of the mixed paraffin fractions were frozen solid and placed in the funnel over a pad of glass wool. As the bath gradually heated up, fractions were drained off by pressing the wax with a glass rod. This apparatus was discarded because sufficiently low temperatures could not be obtained.

The next apparatus used was an electrically heated and dry ice cooled funnel (Fig. 2b) similar to the one used in the first apparatus.

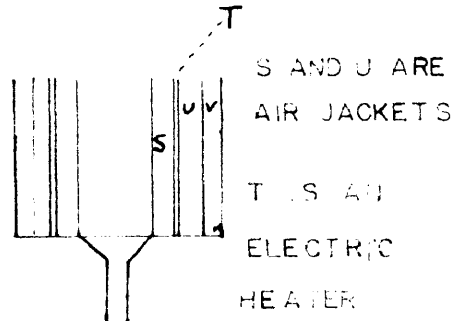
TABLE II
RESULTS OF EQUILIBRIUM MELTING

Boiling range °C	Fraction	Wt. Gms. after H_2SO_4 Treatment	Temp. of Bath °C	Refr. Ind.	M.P.-S.P. After H_2SO_4 Treatment
200-207	18	0.5	47.6	1.4415	57, 57
	19	0.4	51.8	1.4410	57, 56.8
	20	2.2	55.4	1.4370	57, 56.8
	21	4.4	58.0	1.4345	58.5, 58.2
	22	2.0	over 58	1.4342	59.5, 59.0
195-200	3	2.1	50.6	1.4416	56.5, 56.0
	4	1.6	54.0	1.4380	56.3, 56.0
	5	1.7	56.0	1.4360	58.0, 57.5
	6	3.9	58.0	1.4345	58.8, 58.3
	7	4.3	60.0	1.4335	59.3, 58.8
188-195	23	0.6	52.0	1.4399	54.8, 54.5
	24	2.6	54.0	1.4348	55.8, 55.5
	25	7.5	56.0	1.4330	56.5, 56.0
	26	4.4	over 56	1.4329	57.0, 56.8
180-185	27	2.6	51.0	1.4360	54.0, 53.7
	28	6.1	53.0		54.5, 54.0
	29	16.2	55.0		55.0, 54.5
180-200	2	2.8	53.4	1.4360	55.0, 54.5
	1	1.4	over 53.4	1.4324	55.8, 55.2
175-180	8	2.3	48.0	1.4360	51.8, 51.3
	9	2.0	49.6	1.4327	52.0, 51.5
	10	4.0	51.0	1.4315	52.0, 51.5
	11	13.1	52.0	1.4308	52.4, 52.0
	12	9.9	53.0	1.4312	52.5, 52.0
165-175	30	3.6	46.0		49.5, 49.0
	31	10.2	48.5		49.5, 49.0
	32	22.7	50.5		50.3, 49.8
up to 165	33	7.3	43.6		46.3, 45.9
	34	16.0	46.0		47.0, 46.5
	35	17.5	48.0		47.2, 46.8
148-165	36	5.9	44.0		46.2, 45.8
	37	24.0	46.0		46.2, 45.9
	38	3.2	over 46		47.0, 46.4
up to 145	13	2.3	28	1.4392	40.5, 40.0
	14	1.7	32	1.4307	39.0, 38.2
	15	2.4	37.2	1.4310	40.8, 40.6
	16	4.5	39.5	1.4274	41.1, 40.8
	17	12.5	42.5	1.4264	41.8, 41.3

FIG. 2
 APPARATUS FOR
 EQUILIBRIUM MELTING



a.

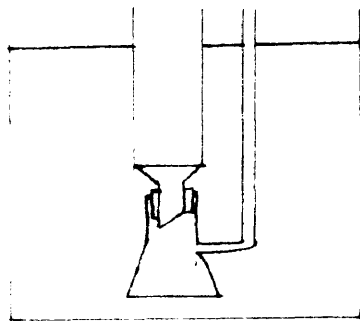


S AND U ARE
 AIR JACKETS

T IS AN
 ELECTRIC
 HEATER

V IS A JACKET
 CONTAINING DRY
 ICE

b.



c.

Temperatures around 0° could readily be obtained but were not very constant.

The apparatus finally adopted for use on all the fractions obtained by fractional distillation is pictured in Fig. 2c. It consisted of the same type of funnel used in the other set-ups, but had a different type of a filter pad. A piece of linen was sewed on to a Knorr extraction plate so that the top of the plate was covered with a smooth surface of linen. About 4-5" of copper wire was soldered on to the attached pin, and the plate fitted snugly into the funnel. The wire was wrapped firmly around the funnel tube to prevent the plate from moving. This type of filter pad was found to be very satisfactory, no solids getting through and the liquid passing through easily. Moreover, the holdup was very small. A piece of heavy nichrome wire passed through a short length of glass tubing inserted in a cork at the mouth of the funnel, and bent in the shape of a circle at the end, served as a stirrer.

After placing 5-30 gra. of a particular fraction in the funnel, it and the attached side-armed Erlenmeyer flask were placed in a constant temperature bath. The Erlenmeyer had a side-arm long enough to extend out of the bath. The funnel was attached to the Erlenmeyer by a tightly fitting rubber stopper. The thermoregulator used was provided with a stopcock which when open allowed the bath to heat up. When any desired temperature was reached, the stopcock was closed and the temperature was maintained as closely as could be read on an Anschütz thermometer. In beginning the fractionation of a sample, the temperature was first raised to the point at which the hydrocarbon mass softened considerably, and then maintained for 15-20 minutes with stirring. At the end of this time, the liquid which had not already filtered through was sucked through by

connecting an aspirator to the side-arm of the Erlenmeyer. The apparatus was then allowed to stay in the bath a further ten minutes to insure getting all the hydrocarbons out that would liquefy at that temperature.

Next, the apparatus was removed from the bath, and a blast of air blown on the rubber stopper to keep water out of the flask when it was opened. The hydrocarbons were melted out of the Erlenmeyer, the flask washed with ether, and the washings added to the melted part. The apparatus was again connected and the temperature allowed to rise until the mixture began to soften again. It was given time to come to equilibrium as before and another fraction drawn off. Each of the fractions taken on distillation was cut into from three to five parts by this system.

Each of the fractions obtained by equilibrium melting was placed in a 125 c.c. Erlenmeyer, mixed with 30-60 c.c. of concentrated sulfuric acid, and heated at 120-130° for three hours by immersion in an oil bath heated by a Bunsen burner. The neck of the flask was clamped to a ring stand and the mixture electrically stirred. After the three hours were over the mixture was cooled in ice, filtered through fritted glass, and washed with cold water, then with small quantities of cold acetone, taken up in petroleum ether, and filtered. The solvent was evaporated off and the paraffin recrystallized from acetone.

D. Fractional Crystallization.

At first the oxygen-free fractions obtained by the experiments with equilibrium melting were combined on the basis of melting point, fractions "A" to "I" being obtained. "A" melted at about 57° and "I"

at about 41°. Each of these nine fractions was then fractionally crystallized from ethyl ether, and the fractions thus obtained combined on the basis of melting point.

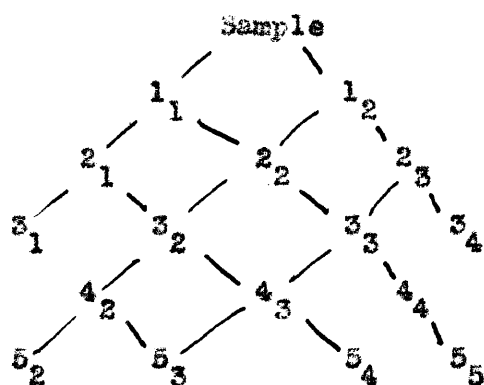
After the fractionation of these nine fractions, it was realized that the best chance for getting anything recognizable out of this obviously complicated mixture was to concentrate on the highest and lowest melting fractions. Repeated fractionation of one of the higher melting fractions, first from ether, then from thirty to sixty degree petroleum ether, gave a product whose physical constants did not change on further fractionation. Fraction R5₄ melted at 60.6-60.8, set at 60.2, and exhibited transition points at 52 and 60.4. These constants were taken using an electrically stirred beaker of oil. Melting points at first taken on a Thiele type, electrically stirred bath were found to be too high by about three degrees. This difference was fairly constant, and was undoubtedly due to insufficient liquid in the bath which caused poor circulation. High melting points have been observed by Sando²³ and others on this type of bath. As soon as it was discovered that the melting points were too high, the bath was discarded and all further melting, set, and transition points were taken on the beaker bath. The results obtained on this apparatus are believed to be very reliable since a calibrated Anschütz thermometer was used, and the rate of heating was slow.

From the lowest melting fraction "I" there was finally obtained, after fractional crystallization from acetone and petroleum ether (1:1), fractions T5₃ and T5₄. The former melted at 41.4, set at 41.1, and exhibited transition points at about 35 and 40.6. The melting point of the latter was 40.0 and it underwent transitions at 35-36 and 39.4. The

constants of C_{21} seemed to fit the straight chain hydrocarbon containing twenty-one carbon atoms, but subsequent examination showed this was not true. Refractionation of some of the fractions intermediate in melting point between the highest and the lowest gave several fractions whose important first transition points on heating were about ten degrees below the melting points. Ordinarily the transition point of a pure hydrocarbon will be four to six degrees below the melting point, while the transition point of a binary mixture may be up to eight degrees below the melting point. However, Chibnall⁵ has shown that a mixture may be essentially binary and yet have a transition point depressed several degrees below the expected temperature, due to the presence of a small quantity of a third substance.

When the dark-colored residue obtained in the fractional distillation was purified by treatment with hot sulfuric acid, and then fractionally crystallized from petroleum ether, several fractions were obtained whose transition points were fairly close to their melting points. Fraction R 18 melted at 65.2° , set at 65.0° , and underwent transitions at 56.2 and at 65.0° .

The procedure used in the fractionation consisted first in dissolving the mixture in the solvent, and then placing it in the ice box. An attempt was made in each crystallization to adjust the quantity of solvent and time of crystallization so that about half the material appeared in the filtrate and half in the precipitate. After crystallization, which took only about ten minutes, the mixture was filtered on a coarse fritted glass filter using gentle suction. The following is a diagram of the general procedure for the fractionations:



Fractions 3_1 and 5_2 were generally found to have almost exactly the same melting points and were combined. Similarly 3_4 and 5_5 were the same. The original sample is first split into a filtrate 1_2 and a precipitate 1_1 . The precipitate always appears on the left in the diagram and the filtrate on the right. The filtrate 2_2 from the crystallization of 1_1 was combined with the precipitate obtained by cooling or concentrating 1_2 . In these fractionations the use of 125 c.c. Erlenmeyers with interchangeable ground glass joints was found to be extremely convenient, as a condenser with ground joint could be connected directly to the flask for concentration purposes. The use of ground joints also avoided contamination of the fractions, which is important in a process such as this.

In the following report of the actual crystallizations which were carried out, the letter in any fraction is the letter given to the starting product of any series of fractionations, and the numbers and subnumerals show the position in a diagram like that on this page. Thus, the name of a fraction $A5_4$ will indicate that fraction A has been crystallized according to the scheme outlined until the place indicated by 5_4 has been reached. A fraction $T5_4$ would be a part of "T" carried to the same place in the general scheme. The large number always indicates the level of the fractionation triangle, while the subnumeral indicates the number of the fraction at that level.

Fractions 18, 19, 2-, and 26, melting at 57°, which were obtained from the experiments with equilibrium melting, were combined, and given the designation "A." Hereafter, fraction numbers given without letters will be fractions obtained from equilibrium melting. Fractionation from ether gave four fractions with the following melting and set-points:

Fraction	A3 ₁	A3 ₂	A3 ₃	A3 ₄
M.P.	59.0	59.0	57.5	55.0
S.P.	58.5	57.5	57.0	-----

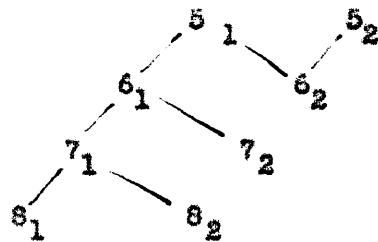
The two fractions A3₁ and A3₂ were not combined, but were fractionated as part of the general scheme down to the fifth level, just as 3₂ and 3₃ were treated in the general diagram on the preceding page. This process of taking only two of the fractions from one level to a lower one will be referred to hereafter as "dual fractionation".

The melting and set-points of the four fractions thus obtained are given in the following table:

Fraction	A5 ₁	A5 ₂	A5 ₃	A5 ₄
M.P.	59.5	59.	57.1	55.
S.P.	59.	58.5	56.9	-----

A3₃ was added to A5₃ and A5₄ was added to fraction 2.

Fractions A5₁ and A5₂ were fractionated as follows:



Actually the filtrates from A5₁ and A5₂ were combined to give A6₂ while the precipitates from these same two fractions were combined to give A6₁.

Next, the most insoluble fraction A6₁ was crystallized a number of times to give precipitate A9₁, then A10₁, then A11₁, then A12₁; and

filtrates A9₂, A10₂, A11₂, and A12₂.

The constants for A11₁ and A12₁ were as follows:

Fraction	A11 ₁	A12 ₁
M.P.	60.7	60.8
S.P.	60.2	60.3

Two more crystallizations of A12₁ gave A14₁ melting at 61.1.

The two filtrates were combined with A12₂.

The constants for the filtrate obtained were as follows:

Fraction	A12 ₂	A11 ₂	A10 ₂	A9 ₂
M.P.	60.5	60.0	59.9	59.9

Fraction	A8 ₂	A7 ₂	A6 ₂
M.P.	59.9	59.	58.

Fractions A11₂, A10₂, A9₂, A8₂, A12₂, and 22 were combined.

Thus, from these fractionations of "A", the following six fractions were left:

Fraction	A3 ₄	A5 ₃	A14 ₁	A8 ₂	A7 ₂	A6 ₂
M.P.	55.	57.1	61.1	Ca. 60	59.0	58.0

The next step was to combine fractions 1, 3, 4, 24, and 25.

These fractions melting at 56-56.5 were called "B". Fractionation from ether yielded the following fractions:

Fraction	B3 ₁	B3 ₂	B3 ₃	B3 ₄
M.P.	58.5	57.0	57.0	56.

Fraction A5₃ and B3₃ were added to B3₂. Fractions B3₁ and B3₂ were then "dually fractionated" as was "A". The following fractions were obtained:

Fraction	B6 ₁	B6 ₂	B6 ₃	B6 ₄	B6 ₅
M.P.	58.8	58.	57.	55.3	52.

B6₁ was added to A7₂, B6₂ was added to A6₂, and B6₅ was added to fraction 10.

Thus, from "B", fractions B6₃ and B6₄ were left.

Next, fraction "C" melting at about 55° was formed from fractions 23, 29, 2, and B6₄. The usual fractionation from ether resulted in the following four fractions:

Fraction	C3 ₁	C3 ₂	C3 ₃	C3 ₄
M.P.	56.5	56.0	54.7	52.5

Dual fractionation of C3₂ and C3₃ gave the following fractions:

Fraction	C6 ₂	C6 ₃	C6 ₄	C6 ₅	C6 ₆
M.P.	57.0	56.0	55.3	53.8	52.2

B6₃ and C3₁ were combined with C6₂, and A3₄ was added to C6₄.

Next, "D", melting at 54-54.5, was formed by combining fractions 27, 28, and C6₅. The usual fractionation down to the third level, and dual fractionation of D3₂ and D3₃ to the level of four gave the following:

Fraction	D3 ₁	D4 ₂	D4 ₃	D4 ₄	D3 ₄
M.P.	56.	55.5	54.	52.	----

B3₄ was added to D4₃, D3₁ was added to C6₃, and D4₂ was added to C6₄.

Next, "E" melting at 51.8-52.5 was formed from the combination of fractions 8, 9, 10, 11, 12, D4₄, D3₄, C3₄, and C6₆. Fractionation of "E", with dual fractionation of E3₂ and E3₃ gave the following:

Fraction	E3 ₁	E6 ₂	E6 ₃	E6 ₄	E6 ₅	E6 ₆	E3 ₄
M.P.	54.0	54.0	53.0	52.2	51.0	50.0	----

E3₁ and E6₂ were added to D4₃.

Next, "F", melting at 49.5-50.3, was formed from fractions 30, 31, 32, E6₆, and E3₄. Fractionation of "F" and dual fractionation of F3₂ and F3₃ gave the following:

Fraction	F3 ₁	F6 ₂	F6 ₃	F6 ₄	F6 ₅	F6 ₆	F3 ₄
M.P.	51.5	52.0	51.5	50.5	50.0	49.5	49.5

F3₁ and F6₂ were added to E6₄.

Fraction F6₄ was the first fraction in which transition points were observed. The transition points on heating were 38 and 50°.

Fraction "G", melting at 47°, was next formed from fractions 34, 35, and 38. The following fractions were obtained in the usual way:

Fraction	G3 ₁	G3 ₂	G3 ₃	G3 ₄
M.P.	49.	49.	47.	46.6

Dual fractionation of G3₂ and G3₃ resulted in the following:

Fraction	G5 ₂	G5 ₃	G5 ₄	G5 ₅
M.P.	49.	48.	47.	46.
2nd T.P. on heating	48.2	47.	----	45.

Fractions F3₄, F6₆, G3₁, and G5₂ were combined.

Next, fraction "H", melting at 46°, was formed from fractions 33, 36, 37, G3₄, and G5₅. Fractionation of "H" and dual fractionation of H3₂ and H3₃ gave the following:

Fraction	H3 ₁	H5 ₂	H5 ₃	H5 ₄	H5 ₅	H3 ₄
M.P.	48.	47.5	47.	46.	45.	45.5
2nd T.P. on heating	47.	47.	46.	45.	----	44.

H3₁, H5₂, and H5₃ were combined with G5₄; and H5₅ and H3₄ were combined.

The next step was to combine fractions 13, 15, and 16 to give

"I", melting at 41°. Fractionation gave the following:

Fraction	I3 ₁	I3 ₂	I3 ₃	I3 ₄
M.P.	43.	42.	41.2	39.8
2nd T.P. on heating	42.	41.	40.	39.

To I3₂ was added fraction 17, and fraction 14 was added to I3₄.

The next step consisted of refractionation of suitable fractions already obtained. Fraction A8₂ melting at 57 was re-named "J" for the sake of convenience, and refractionated to the level of three, and then J3₂ and J3₃ were dually fractionated giving the following:

Fraction	J5 ₁	J5 ₂	J5 ₃	J5 ₄	J5 ₅	J3 ₄
M.P.	60.5	60.	59.	58.	56.	56.

J5₃ was added to A3₂, J5₄ was added to A6₂, and J3₄ and J5₅ were added to C6₃.

J₃₁ and J₅₂ were combined and called "K". Refractionation of "K" with dual fractionation of K₃₂ and K₃₃ gave the following:

Fraction	K ₃ ₁	K ₄ ₂	K ₄ ₃	K ₄ ₄	K ₂ ₃
M.P.	60.5	60.5	59.5	57.5	57.

K₄₃ was added to A₇₂, and K₂₃ and K₄₄ were added to A₆₂.

K₃₁ was re-named "M" and fractionated to give the following:

Fraction	M ₃ ₁	M ₃ ₂	M ₃ ₃	M ₂ ₃
M.P.	61.7	61.	60.	59.

M₂₃ was added to A₇₂, and M₃₁ was further fractionated to give the following:

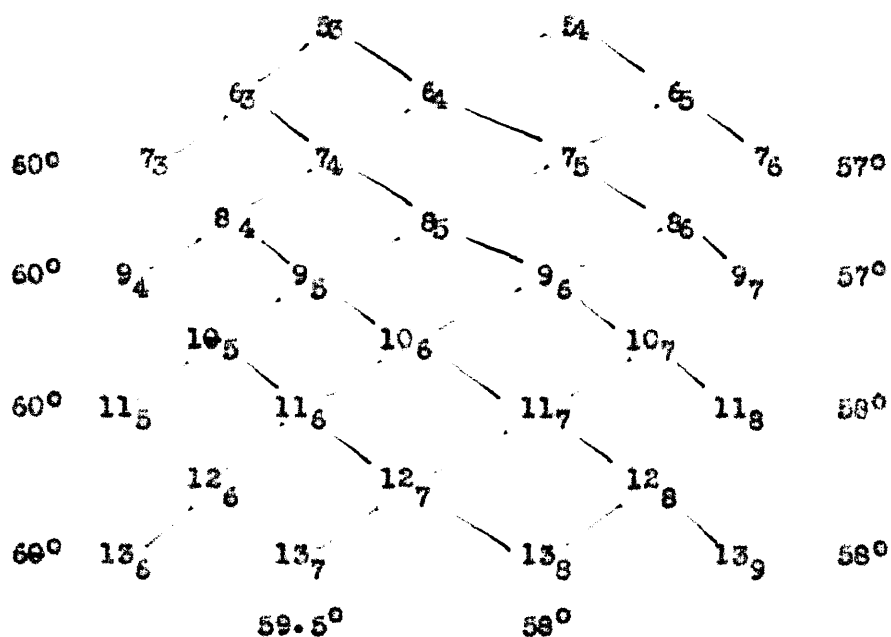
Fraction	M ₆ ₁	M ₆ ₂	M ₆ ₃	M ₆ ₄
M.P.	62.	61.5	60.5	60.

M₆₃ and M₆₄ were added to M₃₃.

Next A₆₂, renamed "L" and melting at 59° was fractionated and A₃₂ and A₃₃ were dually fractionated to give the following:

Fraction	L ₃ ₁	L ₅ ₂	L ₅ ₃	L ₅ ₄	L ₅ ₅	L ₃ ₄
M.P.	60.	60.	---	---	57.	57.

L₅₃ and L₅₄ were fractionated according to the following scheme (the melting points are given adjacent the fractions):



$L3_1$, $L5_2$, $L7_3$, $L9_4$, $L11_5$, and $L13_6$ were now combined and called "N". On carrying out a series of fractionations like the previous series, the following fractions were obtained:

Fraction	$N3_1$	$N3_4$	$N5_2$	$N5_5$	$N7_3$	$N7_6$
M.P.	61.	59.	61.	59.	61.	59.
Fraction	$N9_4$	$N9_5$	$N9_6$	$N9_7$		
M.P.	61.	59.5	59.	---		

$N5_5$, $N7_6$, $N9_5$, $N9_6$, and $N9_7$ were added to $N3_4$. $N3_1$, $N5_2$, $N7_3$, and $N9_4$ were combined and called "O". Refractionation of "O" to the level of three and then dual fractionation of $O3_2$ and $O3_3$ gave:

Fraction	$O3_1$	$O3_2$	$O3_3$	$O3_4$	$O3_5$	$O3_6$
M.P.	61.	61.	60.	60.	---	59.8

Fractions $O3_3$ and $O3_4$ were added to $O3_4$.

$O3_1$ and $O3_2$ were combined and called "P". Fractionation of "P" according to the same scheme as the last series of fractionations gave:

Fraction	$P3_1$	$P3_2$	$P3_3$	$P3_4$	$P3_5$	$P3_6$
M.P.	61.	61.	60.5	60.	60.	60.

$P3_3$ also underwent a transition at about 52° .

$P3_1$ and $P3_2$ were combined, called "Q", and fractionated again in the same manner as the foregoing to give:

Fraction	$Q3_1$ and $Q3_2$	$Q3_3$	$Q3_4$	$Q3_5$ and $Q3_6$
M.P.	61.	61.	61.	61.
S.P.	61.	60.3	ca. 52	---
T.P. (1st)	50.	52	---	ca. 52
T.P. (2nd)	61.	---	---	---

After treating $Q3_1$ and $Q3_2$ with sulfuric acid the following constants were obtained: M.P. 61.8, S.P. 61.0, and T.P. 53.

The next step was to change the solvent. $Q3_3$, $Q3_4$, and $Q3_5$ were combined, called "R", and fractionated from $30-60^\circ$ petroleum ether, according to the same scheme as the last series of fractions. The

following fractions were obtained:

Fraction	R3 ₁ and R5 ₂	R5 ₃	R5 ₄	R5 ₅ and R 3 ₄
M.P.	61.2	61.	60.6 - 60.8	60.2
S.P.	60.9	---	60.2	---
T.P. (1st)	53.	53.	52.	52.
T.P. (2nd)	61.	---	60.4	---

Since it appeared that appreciable changes in the constants were no longer taking place, further fractionation of this material was abandoned.

Next, the fractions I3₁, I3₂, I3₃, and I3₄ were purified with sulfuric acid, and their physical constants carefully determined:

Fraction	I3 ₁	I3 ₂	I3 ₃	I3 ₄
M.P.	42.7	41.6	41.2	39.5
S.P.	42.4	41.0	40.4	38.8
T.P. (1st)	below 31	ca. 35.	34.	ca. 30.
T.P. (2nd)	42.0	40.6	40.6	---

Fraction I3₂ was renamed "S" and fractionated from petroleum ether-acetone (1:1) according to the scheme used in the last several series. The following fractions were obtained:

Fraction	S3 ₁ and S5 ₂	S5 ₃	S5 ₄	S5 ₅ and S3 ₄
M.P.	43.4	42.0	41.0	39.
S.P.	42.8	41.8	---	38.8
T.P. (1st)	35.2	under 30	36.5	---
T.P. (2nd)	43.2	ca. 41.5	---	---

Next, S5₄ was called "T" and carried through a series of fractionations from acetone-petroleum ether (1:1) with the following results:

Fraction	T3 ₁ and T5 ₂	T5 ₃	T5 ₄	T5 ₅ and T3 ₄
M.P.	42.5	41.4	40.0	38.8
S.P.	---	41.1	---	---
T.P. (1st)	36.	ca. 35.	35.-36.	33.
T.P. (2nd)	42.	40.6	39.4	---

Fraction F6₃ was next selected for refractionation. Careful determinations of its constants gave for the melting point 50.2, set-point 49.4; and transition points 37-38 and 49.6. The following

fraction were obtained from petroleum ether-acetone (1:1):

Fraction	U3 ₁	U3 ₂	U3 ₃	U3 ₄
M.P.	51.0	50.6	49.2	47.8
S.P.	50.6	49.8	48.9	47.4
T.P. (1st)	39.	37.4	ca. 39.	ca. 38.-39.
T.P. (2nd)	50.4	49.8	48.2	47.2

Next, G6₄ was called "V" and its constants carefully determined. They were: melting point 55.6, set-point 55.1, and transition points 42. and 54.8. Fractionation from acetone-petroleum ether gave the following:

Fraction	V3 ₁	V3 ₂	V3 ₃	V3 ₄
M.P.	56.6	56.2	55.2-55.4	----
S.P.	56.2	55.8	55.0	----
T.P. (1st)	45.	44.6	43.0	below 39
T.P. (2nd)	----	55.2 - 54.8	----	----
		55.4		

V3₂ was renamed "W" and further fractionated to give the following:

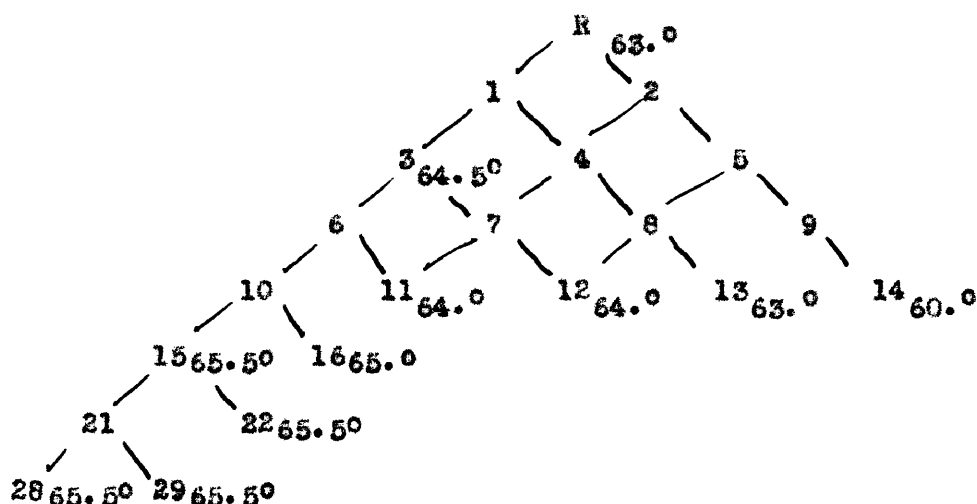
Fraction	W3 ₁	W3 ₂	W3 ₃	W3 ₄
M.P.	56.8	56.4-56.6	55.6	53.8
S.P.	56.3	54.9	55.2	53.4
T.P. (1st)	44.4-45.6	45.2	44.7	ca. 45
T.P. (2nd)	56.0	56.0	55.2	53.0

W3₂ was renamed "X", and further fractionated to the level of three, and fractions X3₂ and X3₃ were dually fractionated to give the following:

Fraction	X3 ₁ and X5 ₂	X5 ₃	X5 ₄	X5 ₅ and X3 ₄
M.P.	56.6-56.7	55.8	55.6	55.0-55.2
S.P.	56.3	55.4	55.1	54.4-54.6
T.P. (1st)	46.0	44.6-44.8	43.8	42.
T.P. (2nd)	56.4	55.6	55.0	54.6

Fractionation of the still residue. The still residue was called "R" and fractionated from petroleum ether. It will be noted that previously the letter "R" was used unintentionally, for an entirely different fraction. The two different R's may be distinguished by the numbers which follow the letter. In the fractions derived from the still

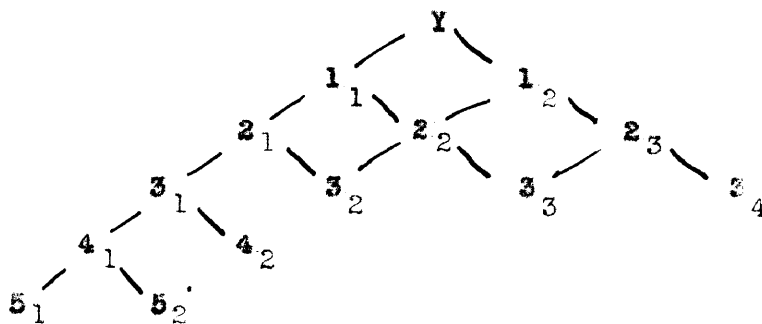
residue, no subnumerals are used, while in the "R" which appeared previously in the thesis, one number to represent the fractionation level, and a subnumeral to represent the number of the fraction in the level were used. In the following diagram the melting points appear adjacent the fraction numbers:



R12 was combined with R11; and R28, R29, and R22 were combined with R16. Careful determinations of the constants for R16 and R11 gave the following results:

Fraction	M.P.	S.P.	T.P. (1st)	TiP. (2nd)
R16	65.2	65.0	56.2	65.0
R11	64.2	63.8	54.0	63.0

Fractionation of R11 called "Y", from petroleum ether, was carried out according to the following diagram:



The constants for the fractions obtained were as follows:

Fraction	Y5 ₁	Y5 ₂ and Y4 ₂	Y3 ₂	Y3 ₃
M.P.	65.8	64.4	63.7-63.9	ca. 63.4
S.P.	65.2	63.8	63.4	-----
T.P. (1st)	55.-56.	54.-55.	53.-54.	indef.
T.P. (2nd)	65.2	63.8	63.0	-----

2. Melting, transition, and set-points.

The bath used for the careful determination of these constants was a 250 c.c. beaker, containing about 200 c.c. of cottonseed oil and heated by a Bunsen burner. The liquid was stirred well by an electric stirrer. A Bureau of Standards calibrated Anschütz thermometer graduated in 0.2° divisions was placed in the center of the bath, and read with the aid of a small lens of magnification about x3. Immersion was about fifty per cent. In order to cool the bath rapidly, ice was placed on the wire gauze around the beaker. In this way it was easy to check the transition point which is difficult to observe in many cases, and must be taken several times before a definite value is determined. Open capillary tubes were used; no difference was observed between these results and those obtained by using sealed tubes. The wax was pushed down the tube by means of a glass rod to a height such that when melted it was two to three millimeters. The tube was then placed on the steam bath for a minute until all the air bubbles were expelled, and then put in the melting point bath next to the thermometer. The bath was heated above the melting point of the sample and allowed to cool slowly until it solidified, and then cooled with ice below the transition point. The bath was then heated slowly to the transition point which was recorded, then more rapidly to a point about two degrees below the melting point. The paraffin underwent another transition about a half degree below the melting point and finally melted sharply to a clear liquid. On slow cooling the setting temperature was ascertained.

The transition points for the lower paraffins were not so definite as those of the higher members. The material appeared somewhat glassy at room temperature but a number of cracks or fissures were noted. At the transition point, the entire material became clear except for a smooth, elongated air bubble in the center. In some cases, especially if sufficient time was not given for the sample to change from one state to another the air bubble persisted when the sample was cooled below the transition point, but jagged edges appeared in it. On raising the temperature to the transition point the edges smoothed out. The second transition point on heating was marked by a disappearance of the air gap, and the changing of the material from a glassy to an opaque state. The set-point was taken as that temperature at which needles appeared in the liquid. The values reported for the transition points, set points, and melting points are believed to be good to 0.2° .

Calibration of melting point bath.

Found for nonacosane^{*}:
 M.P. 63.6 - 63.8
 S.P. 63.1
 T.P.'s 56.8, 63.4

Chibnall's values:
 M.P. 63.4 - 63.6
 S.P. 63.2
 T.P.'s 57.3 - 57.5, 63.2

F. X-ray spacings.

The spacings were obtained by using a G.E. Hayes X-ray diffraction unit with a self-rectifying Phillips "chrome-iron" research diffraction tube, having a copper target. The tube was water-cooled and operated at 30 K.V. and 20 m.a. A "circular reflection" camera was used with the sample mounted on a flat piece of glass in the center. The sample was

^{*} Kindly furnished by C.E. Sando of the United States Department of Agriculture

either melted on or the crystals pressed on to the glass. The x-ray beam entered through a narrow slit, striking the sample, which was oscillated through about 36° , at grazing incidence. The wave length of the radiation used was 1.539 \AA . The film was bent in an arc around the circumference of the camera, allowing registration over about 200° . The radius of the camera was $5.945 \pm .005 \text{ cm.}$

The film was measured to 0.01 cm. with a scale and vernier. By using the weighted average of from four to thirteen orders, the values for "D," the distance of the first order reflection from the undeviated beam was determined to within 0.002 cm. Usually the number of orders present was greater than the number measured, for only those were used in obtaining the average values that were clear enough to measure accurately. The overall accuracy of the determinations of "d" the interplanar spacing was about one per cent. The accuracy using this apparatus on materials with shorter spacings, i. e. larger angles, was of course much better.

The angle θ in Bragg's law was determined in the usual way by dividing twice the radius into the distance "D" and then multiplying by the conversion factor for degrees to radians.

$$\theta = \frac{D}{2R} \times 57.30$$

θ was then substituted in Bragg's law $n \lambda = 2 d \sin \theta$ to give the interplanar spacing "d".

The actual photographs obtained in this research are given in figs. 3 to 14.

Calibration of X-ray diffraction apparatus.

Found for nonacosane [*] :	
D	= 0.278 cm. (average of 13 orders; sample pressed on to plate)
θ	= $1^{\circ} 8' 53''$
d	= 38.4 \AA
Chibnall's value for nonacosane :	
d	= 38.68 \AA

* Obtained from C. E. Sando of the United States Department of Agriculture

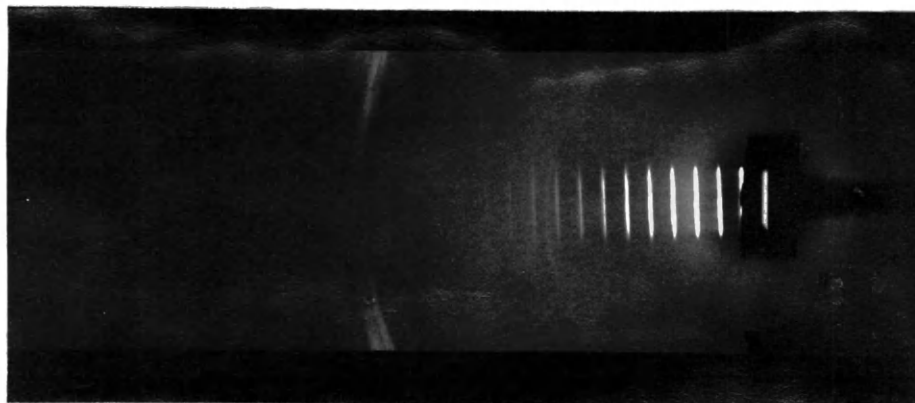


Fig. 3 X-ray Diffraction Pattern of Nonacosane

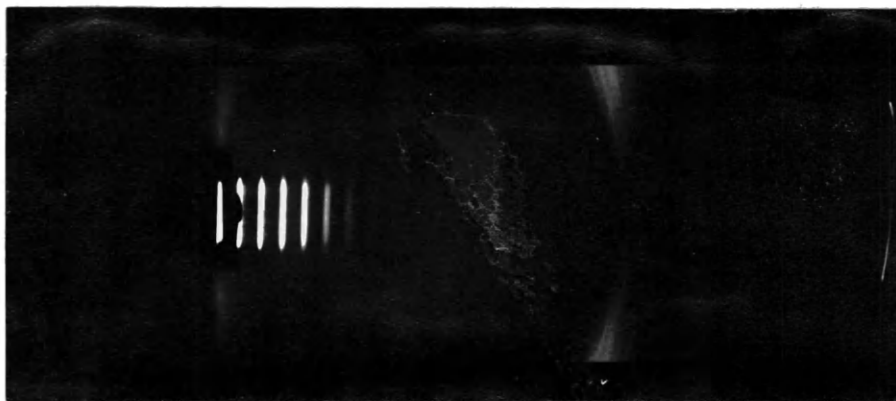


Fig. 4 X-ray Diffraction Pattern of Fraction R 16

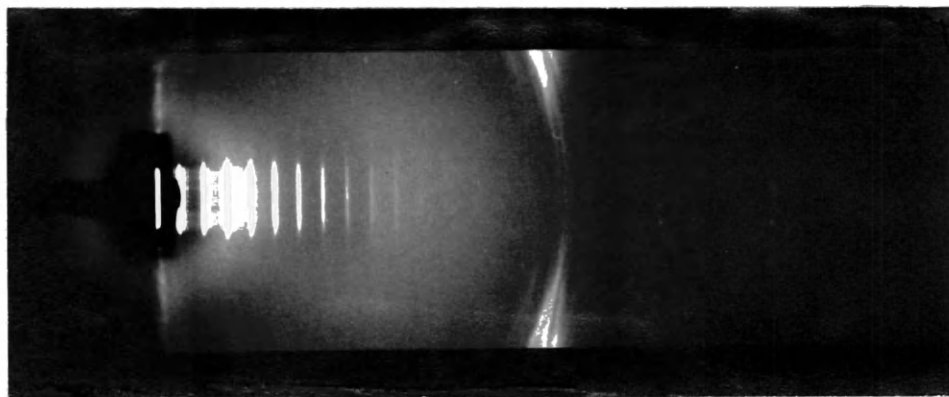


Fig. 5 X-ray Diffraction Pattern of Fraction R54

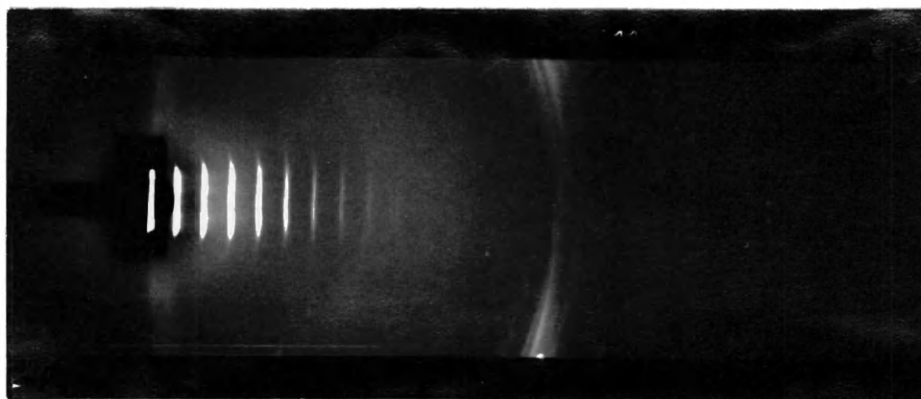


FIG. 6 X-ray Diffraction Pattern of Fraction U33



FIG. 7 X-ray Diffraction Pattern of Fraction X31

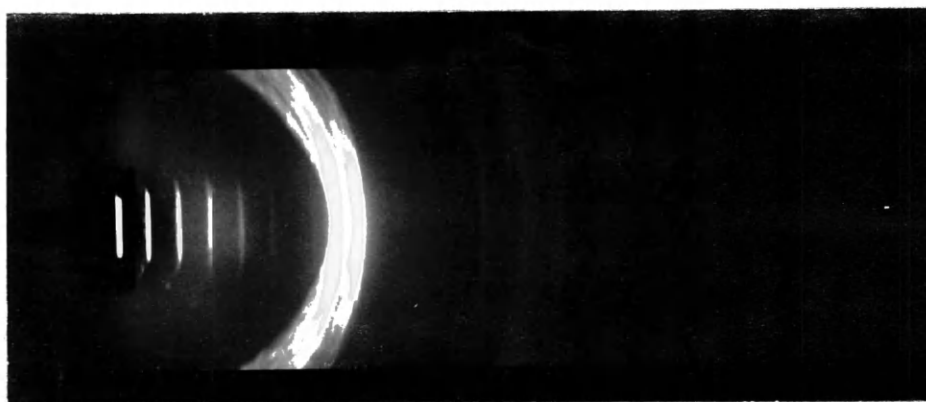


FIG. 8 X-ray Diffraction Pattern of Fraction T53

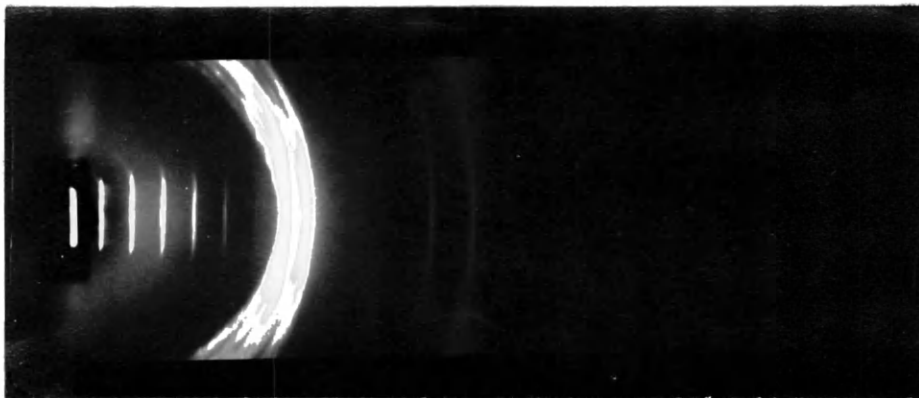


Fig. 9 X-ray Diffraction Pattern of Fraction T5₄ (Melted).

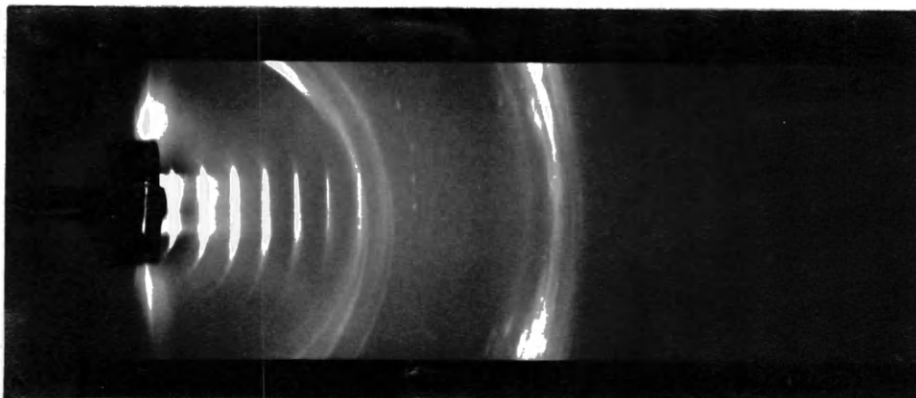


Fig. 10 X-ray Diffraction Pattern of Fraction T5₄ (Pressed).

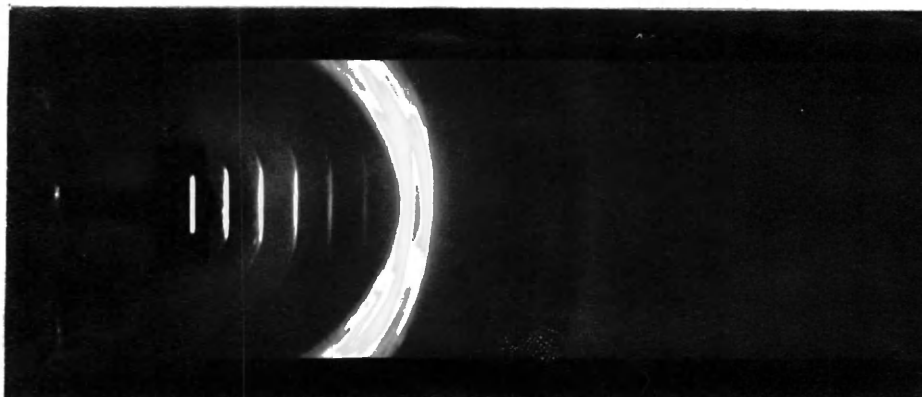


Fig. 11 X-ray Diffraction Pattern of Nonadecane.

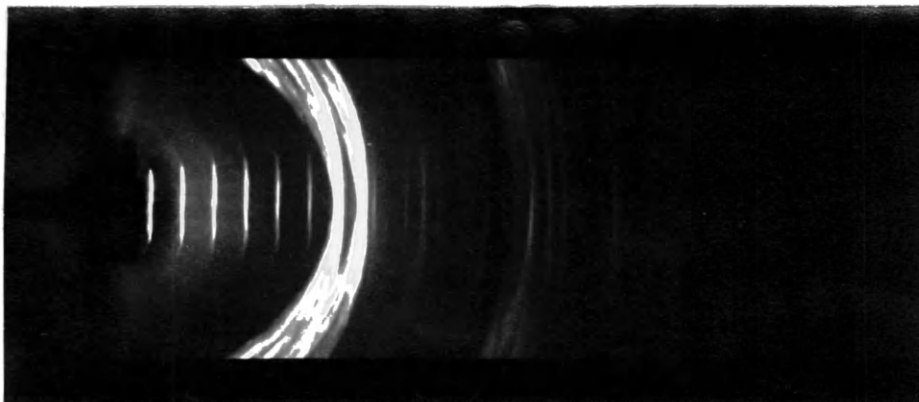


Fig. 12 X-ray Diffraction Pattern of Heneicosane

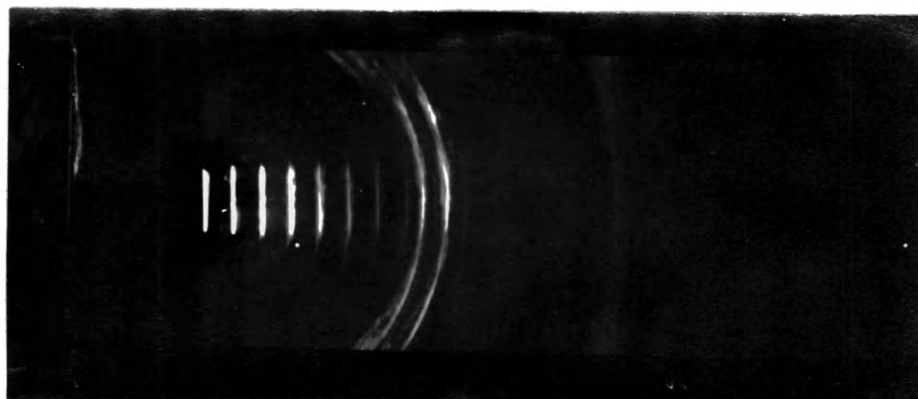


Fig. 13 X-ray Diffraction Pattern of Tricosane

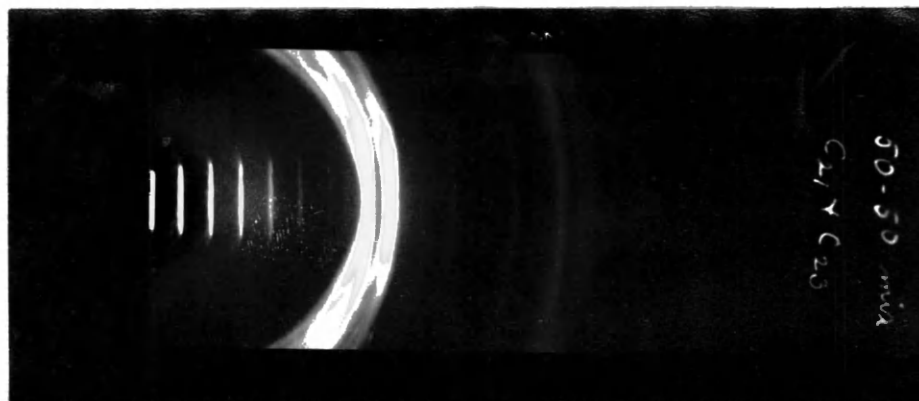


Fig. 14 X-ray Diffraction Pattern of a Mixture of
50% Heneicosane and 50% Tricosane

Sample calculation of spacing.Sample R5₄

Order Number	Units of "D"	Distance from 1st Order Line	
2	1	0.28	Average D = $\frac{10.31}{36} = 0.287$ cm. $\theta = \frac{57.30}{2 \times 6.94} \times 0.287 = 1.184^\circ = 1^\circ 11' 2''$ $d = \frac{1 \times 1.539 \times \sin 1^\circ 11' 2''}{2} = 37.2 \text{ \AA}$
3	2	0.57	
4	3	0.86	
5	4	1.14	
6	5	1.43	
7	6	1.72	
8	7	2.01	
9	8	2.30	
Total	36	10.31	

Summary of Results of X-ray Determinations.

Sample	Orders Measured	Average D in cm.	θ	d in \AA
Synthetic C ₂₁ H ₄₄ (melted)	5	0.380	1° 34' 1"	28.1
T5 ₄ (melted)	5	0.369	Same as pressed sample	
T5 ₄ (pressed flakes)	5	0.370	1° 31' 30"	28.9
R5 ₄ (pressed)	8	0.287	1° 11' 2"	37.24
X3 ₁ (pressed)	7	0.301	1° 14' 24"	35.55
U3 ₃ (pressed)	6	0.330	1° 21' 32"	32.45
T5 ₃ (melted)	4	0.372	1° 32' 2"	28.75
50-50 C ₂₁ H ₄₄ and C ₂₃ H ₄₈ (melted)	4	0.356	1° 28' 5"	30.0
R16 (pressed)	4	0.263	1° 5' 6"	40.64
Synthetic C ₁₉ H ₄₀ (melted)	5	0.410	1° 41' 28"	26.1
Synthetic C ₂₃ H ₄₈ (melted)	7	0.345	1° 25' 16"	31.0

G. Synthesis of hydrocarbons.

It was found that Chibnall⁴ and his co-workers had determined physical constants for a number of hydrocarbons and their mixtures, from hexacosane to pentatriacontane, but had done nothing with the lower members of the series. They did show, however, that the curve for transition points

versus compositions, could be calculated for one mixture, provided the curve for a similar mixture, containing longer or shorter chains, had been determined. Thus, the transition point-composition curve for a mixture of heptacosane and nonacosane would have the same shape as the nonacosane-hentriacontane curve, but would merely have a lower series of ordinates (see fig. 15). However, it was not known how far this process of calculation of constants could be carried, and since some of the mixtures obtained in this research were considerably removed in carbon content from the lowest with which Chibnall worked, it was thought advisable to make several of the lower paraffins and determine their physical constants and the constants of several of their mixtures.

Nonadecane, heneicosane, and tricosane were synthesized by a method similar to that used by Chibnall⁴ and others, with several modifications. The proper long chain acids were pyrolyzed in the presence of reduced iron to give excellent yields of the ketone. When a perforated iron plate such as that used by Chibnall was tried, poor yields were obtained. This may have been due to the difference in the kind of iron used. Chibnall did not specify any particular kind of iron, but the material used in this work was de-galvanized sheet iron. In the reduction of the ketone to the hydrocarbon, the best yields were obtained when zinc amalgam and alcohol saturated with hydrogen chloride were used, and the mixture was heated and mechanically stirred vigorously during the reaction period. The hydrocarbons were freed of any unreacted ketone by treatment with hot sulfuric acid until addition of fresh acid no longer removed color, and were further purified by recrystallizing several times from acetone. The physical constants of the synthetic hydrocarbons and of several mixtures, which were made up in a manner similar to that described by Chibnall, are given in Table III.

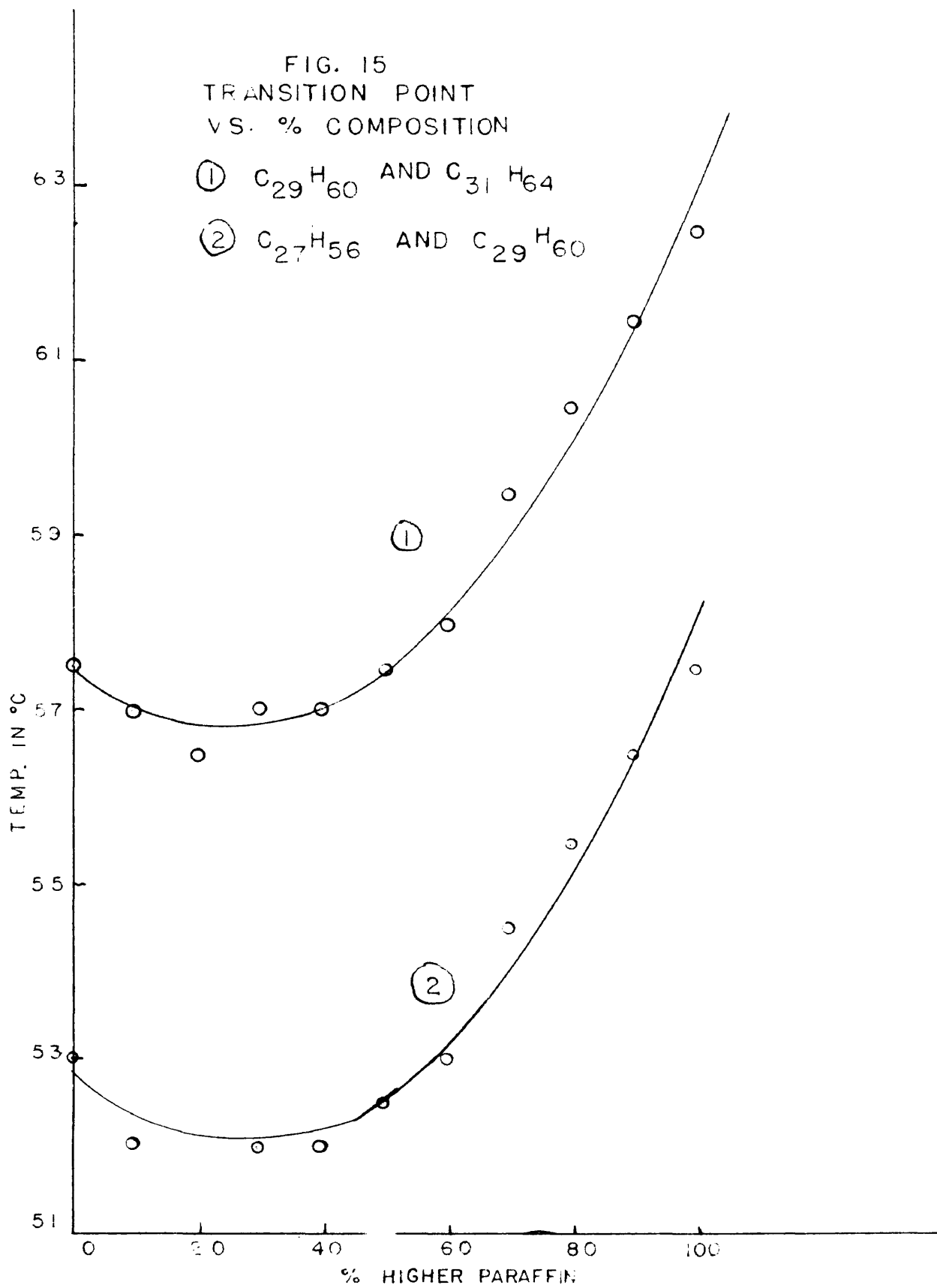
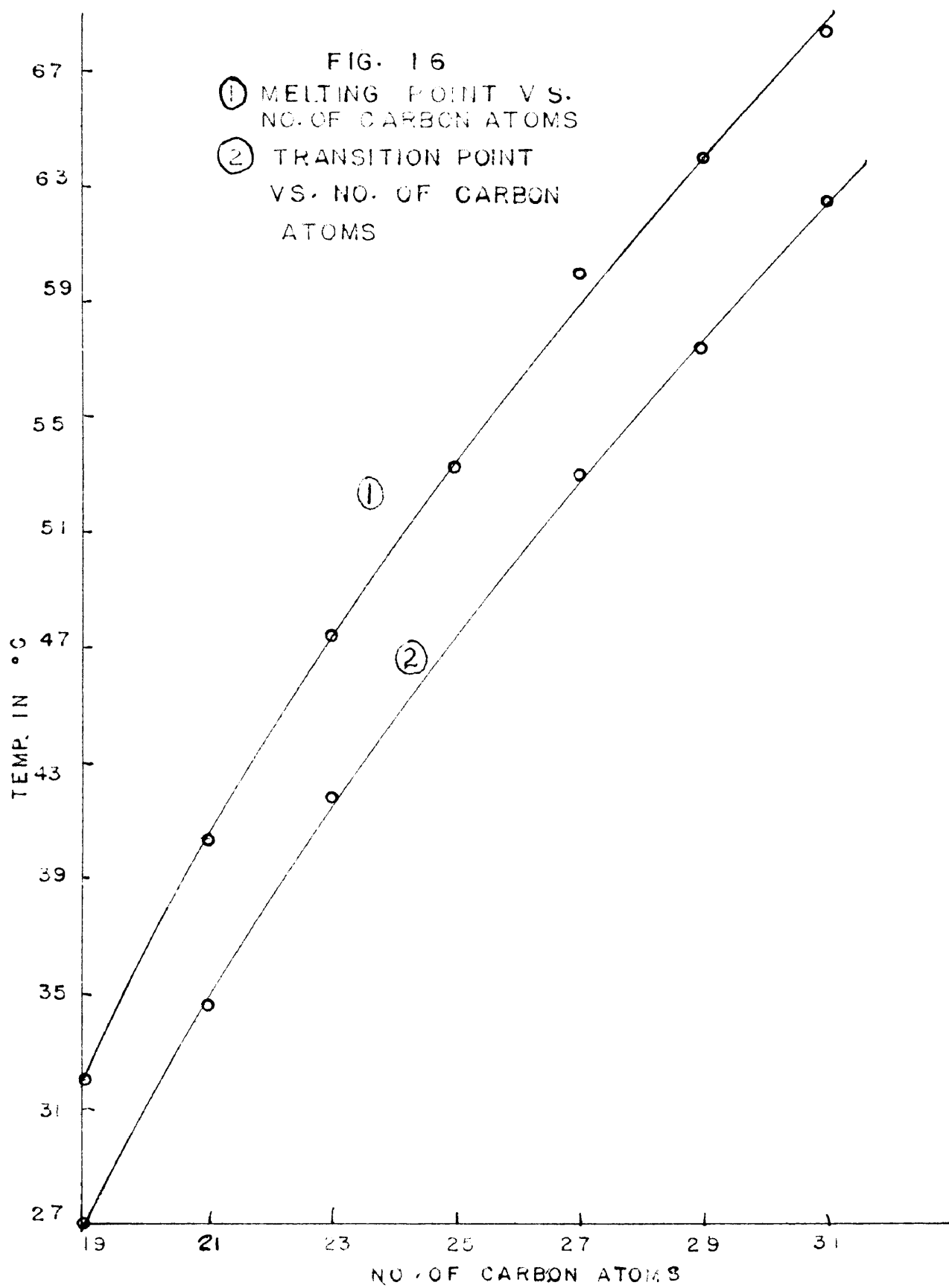
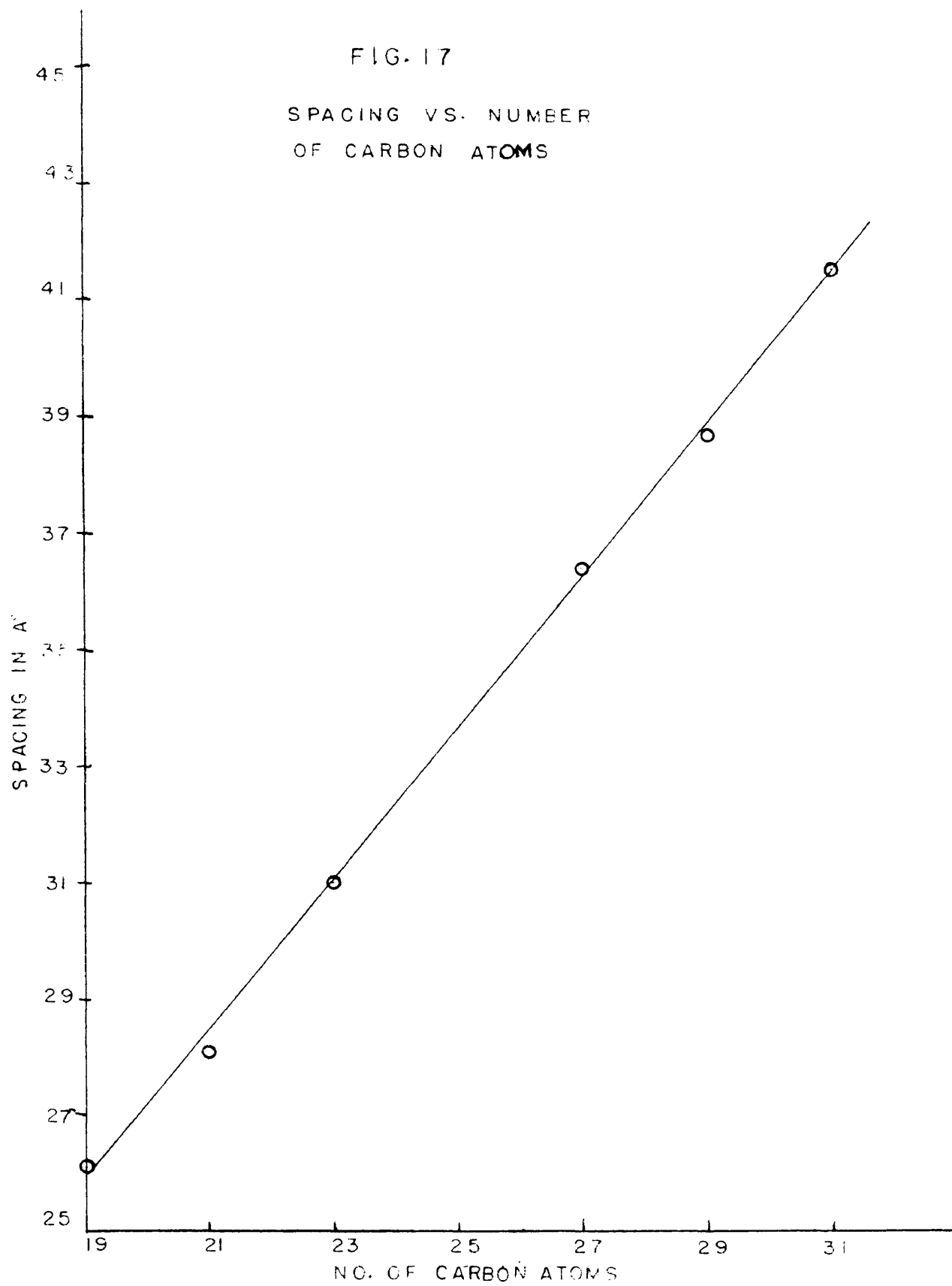


Table III

Sample	M.P. °C	S.P. °C	1st T.P. heating °C	2nd T.P. heating °C	Spacing Å
C ₁₉ H ₄₀	32.0- 32.2	31.5	27.0	31.6	26.2
C ₂₁ H ₄₄	40.2	39.8	34.6	40.0	28.1
C ₂₃ H ₄₈	47.4	47.0	41.6- 41.8	47.2	31.0
50% C ₂₁ and 50% C ₂₃	43.8	43.0	36.6	43.0	30.0
90% C ₂₁ and 10% C ₂₃	40.8	40.4	34.5	40.2	---

It is seen from fig. 16 that the melting points of the pure synthetic hydrocarbons check very closely the "best" values given by Egloff¹⁰, which are thirty-two, forty and four-tenths, and forty-seven and four-tenths degrees for nonadecane, heneicosane, and tricosane, respectively. It is seen from this curve that though a straight line can be drawn through the melting temperatures of the hydrocarbons containing from nineteen to twenty-three carbon atoms, or through the melting points of the homologs containing twenty-seven to thirty-one carbon atoms, there is a definite curvature. Consequently, extrapolation of a straight line through the top points will give erroneous melting points for the lower members of the series. This seems to be true of the transition points of the lower members also. Extrapolation of a straight line through the transition points of the higher members obtained by Chibnall⁴ give values for the lower homologs which are several degrees too high. (see fig. 16) The spacing versus number of carbons, on the other hand, seems to be a perfectly straight line for the whole series. As is seen from fig. 17 the points obtained for the lower members fit closely to the straight line drawn through the spacings of the higher members.





Fractionation of ethyl laurate. Eastman ethyl laurate was purified by fractional distillation through a three foot column packed with glass helices. An electrically heated air jacket had to be kept about 35-40° above the distilling temperature to give smooth distillation without flooding. Fractions were cut by means of a "pig". The middle fraction boiled at 133.7-133.9°/6 mm.

Saponification of ethyl laurate. 44 gms. of the best fraction of the ethyl laurate was saponified by refluxing with a mixture of 250 c.c. of alcohol, 50 c.c. of water, and 5 gms. of sodium for several hours. Acidification to Congo paper with hydrogen chloride, and several recrystallizations from alcohol gave 20 gms. of lauric acid melting at 44°.

Laurone from lauric acid. 3.3 gms. of lauric acid was heated in a pyrex test tube with 0.8 gms. of reduced iron for 3.5 hours at 285° in a salt bath, with occasional stirring. The melt was then extracted several times with boiling alcohol, the solution charcoaled, concentrated, and cooled, whereupon the ketone crystallized in nearly pure form. After several recrystallizations the material melted at 69.0-69.2°. 2.1 gms. of laurone, representing a 75% yield was obtained. Heilbron¹³ gives 69° as the melting point for this compound.

<u>Analysis.</u>	Theory:	C 81.55	H 13.69
	Found:	C 81.33, 81.10	H 13.85, 13.70

Tricosane from laurone. Zinc amalgam was prepared by the Martin²² method. A round-bottomed flask equipped with a ground glass joint was connected to a reflux condenser, at the top of which was a tube through which the hydrogen chloride was led into a running water. 15 gms. of the amalgam was first placed in the flask, then 1 gm. of laurone and 200 c.c. of an acid mixture containing equal volumes of concentrated hydrochloric acid and alcohol saturated with hydrogen chloride gas were added. The mixture was refluxed vigorously for twenty hours, when all the zinc was dissolved. The mixture

was then cooled and filtered. 30 gms. of amalgam and 200 c.c. of fresh acid mixture were then added to the mixture of ketone and hydrocarbon, and the mixture refluxed 9.5 hours. Cooling, filtering off the wax, and crystallization from a mixture of alcohol and petroleum ether gave a product melting at 57-58°. This was treated with concentrated sulfuric acid at 130° several times till fresh acid was no longer colored. Washing with water and crystallization from acetone gave a product melting at 47.4°, which compared well with Strating's²⁴ tricosane which melted at 47.25 - 47.4°. 0.3 gms. was finally obtained.

<u>Analysis:</u>	Theory:	C 86.09	H 14.90
	Found:	C 85.01, 64.61	H 14.80, 14.96

Purification of undecylic acid. Distillation through the same column used for the ethyl laurate gave four fractions, all of which distilled between 150 and 151°. Fraction 3 distilling at 150.8 - 151° was selected for use in synthesizing the ketone.

Didecyl ketone from undecylic acid. 9.5 gms. of undecylic acid and 5 gms. of reduced iron were heated in a glass tube 40 x 230 mm. at 265 - 300° with occasional stirring by means of a glass rod. Working up the melt gave 5.8 gms. of solid melting at 56°. Two crystallizations from methanol gave 2 gms. of ketone melting at 64°. Strating lists the melting point of didecyl ketone as 64.3 - 64.5°.

<u>Analysis.</u>	Theory:	C 81.20	H 13.63
	Found:	C 80.75, 80.39	H 13.72, 13.64

Reduction of didecyl ketone. 0.6 gms. of the ketone, 50 gms. of zinc amalgam, and 150 c.c. of alcohol saturated with hydrogen chloride were refluxed for seventeen hours with two additions of 50 c.c. portions of the acid solution. 0.5 gm. of paraffin melting at 38° was obtained. Treatment

with sulfuric acid gave a product melting at 40.2° . Egloff¹⁰ gives 40.4° as the melting point of heneicosane.

<u>Analysis.</u>	Theory: C 85.01	H 14.95
	Found: C 84.70,	H 15.04,
	84.79	15.11

Synthesis of dinonyl ketone. Eastman capric acid melting at 30° was used without further purification. 15.2 gms. of the acid and 7.5 gms. of reduced iron were heated at $285-295^{\circ}$ for four hours. 7.1 gms. of white solid was obtained melting at 54° . Recrystallization from methanol to constant melting point gave 3.7 gms. melting at $56.0 - 58.2^{\circ}$. Heilbron lists the melting point as 58° .

<u>Analysis.</u>	Theory: C 80.79	H 13.56
	Found: C 80.81,	H 13.58,
	80.54	13.33

Nonadecane from dinonyl ketone. 2 gms. of the ketone, 30 gms. of amalgamated zinc, and 100 c.c. of alcohol saturated with hydrogen chloride were placed in a one-liter three-necked flask, equipped with a reflux condenser and a mechanical stirrer. The mixture was stirred and heated vigorously for twenty-five hours with addition of three 50 c.c. portions of acid and 20 gms. of zinc. 1.5 gms. of hydrocarbon melting at 32° was obtained, representing a yield of 79 per cent. Purification with sulfuric acid gave a product melting at $32.0 - 32.2^{\circ}$. Egloff gives 32° for the melting point of nonadecane.

<u>Analysis.</u>	Theory: C 85.00	H 15.02
	Found: C 85.43,	H 15.20,
	85.20	15.15

SECTION III

CONCLUSIONS

Since the paraffin mixture reacted neither with bromine in carbon tetrachloride nor potassium permanganate, it was evident that no double bonds were present. Carbon and hydrogen analyses showed the substance was a hydrocarbon, and moreover, belonged to the aliphatic series. The percentage composition for all the higher members of the series are approximately the same, since the two end groups do not affect the analyses to any extent, and the carbon and hydrogen contents of these compounds are roughly that of a methylene group in each case. To show whether the substance was a pure compound or a mixture, a cooling curve was obtained. As was evident from fig. 1, page 15, the material was quite definitely a mixture. There was a break in the curve at about fifty degrees, indicating the substance had started to crystallize, but a horizontal plateau was not obtained, the approximately flat portion of the curve covering a range of about a degree and a half.

As was expected from the cooling curve of the original hydrocarbon mixture, the separation of individual homologs was extremely difficult, and in fact, impossible. Despite the fact that a fairly large quantity of the starting mixture was subjected to a systematic separation by fractional distillation, equilibrium melting, and finally by about three hundred crystallizations in a scheme of fractional crystallization, only a partial separation could be achieved. It was possible, however, to obtain a number of fractions which were essentially binary mixtures with probably small quantities of a third component present. Using the methods of Chibnall

and Piper, the compositions of these fractions were interpreted with reasonable certainty. The interpretations were based on Chibnall's hypothesis that only odd-numbered hydrocarbons are present in natural sources. The properties of the fractions obtained in this research bore out this assumption. Thus fraction R5₄ had a melting point and spacing very close to those of octacosane, and before Chibnall's work might have been considered a pure or nearly pure compound. However, it can be said quite definitely it was a mixture of heptacosane and nonacosane, since the transition point was depressed about three degrees below that of the pure compound. Moreover, the x-ray diffraction pattern was not that of a pure compound, but exhibited fewer orders of reflection. The homologs in this mixture could not be separated by more than two carbon atoms because of the combination of sharpness of melting point, and nearness of set-point and second transition on heating to the melting point. Also, since only one set of lines appeared on the photographic plate, the homologs could not be separated by four or more carbon atoms.

In Table IV the physical constants of representative fractions obtained are given, together with the constants for suggested mixtures. The actual percentages estimated are approximate, but there seems little doubt about which homologs were present mainly in the fractions selected for examination. The method used in estimating the composition of mixtures was first to select mixtures with the spacing within one percent of that obtained for the cork fraction. Then that mixture was chosen whose melting point and transition point were in best agreement with the constants of the unknown.

The physical constants for the suggested mixtures agree fairly well for the best of the higher fractions R16 and R5₄. The transition

point of X₃₁ is depressed considerably, but the melting point and spacing agree well with the mixture suggested. Fraction U₃ and T₅, however, had melting points somewhat lower than the spacings would indicate. This probably denotes the presence of a small quantity of branched chain hydrocarbons, although the difference may be within the limit of error of the melting point and spacing determinations. The presence of oxygenated compounds or of unsaturated compounds is not believed likely, since the samples were purified by long treatment with sulfuric acid at one hundred and twenty to one hundred and thirty degrees. Transition points of mixtures not actually determined were obtained from graphs similar in shape to those which have been run, but with different scales of ordinates.

TABLE IV

Sample	M.P.	S.P.	1st T.P. heating	2nd T.P. heating	Spacing Δ°
R 16	65.2	65.0	56.2	65.0	40.6
60% C ₂₉ H ₆₀ 40% C ₃₁ H ₆₄	64.8- 65.0	64.4	56.5- 57.0	----	40.9
R ₃₄	60.6- 60.8	60.2	52.0	60.4	37.2
60% C ₂₇ H ₅₆ 40% C ₂₉ H ₆₀	60.8	----	52.2	----	37.3
X ₃₁	56.6- 56.7	56.3	46.0	56.4	55.55
60% C ₂₇ H ₅₆ 40% C ₂₅ H ₅₂	56.8	----	48.0	----	35.3
U ₃	49.2	48.9	ca. 39	48.2	32.45
60% C ₂₃ H ₄₈ 40% C ₂₅ H ₅₂	49.8	----	ca. 41.2	----	32.3
T ₅	41.4	41.1	ca. 35	40.6	28.75
20% C ₂₃ H ₄₈ 80% C ₂₁ H ₄₂	41.6	----	ca. 35	----	28.7
T ₅	40.0	----	35.0- 36.0	39.4	28.9

The results are believed to show quite definitely the presence of all the odd-numbered hydrocarbons containing from twenty-one to thirty-one carbon atoms in the molecule.

SECTION IV

SUMMARY

1. The literature concerning the isolation and identification of long straight chain hydrocarbons from natural sources has been reviewed.
2. The literature concerning the synthesis of straight chain hydrocarbons has been reviewed.
3. Nondecane, heneicosane, and tricosane have been synthesized. Their physical constants and the constants of several of their mixtures were determined.
4. A new apparatus for equilibrium melting has been developed.
5. The hydrocarbon mixture from a distillate obtained during the preparation of cork board has been separated into a number of fractions which were identified by means of melting points, transition points, and long crystal spacings. All the odd numbered straight chain hydrocarbons containing from twenty-one to thirty-one carbon atoms were found.

SECTION V

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