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STUDY OF THE CRYSTAL BEHAVIOR OF HYDROCARBONS[1]

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ABSTRACT

The construction and operation of a microscope for the observation of the growth of crystals at low temperatures are described. Photomicrographs of nine aromatic, six cycloparaffinic, eight normal paraffinic, and five branched-chain paraffinic hydrocarbons of known structure were obtained. It was shown that successive members of the homologous series of normal paraffins did not differ in crystal appearance. It was observed, however, that condensed molecules tended to crystallize in polyhedrons of about equal dimensions, whereas molecules with long chains tended to form long prisms. Mixed molecules showed modified forms depending on the relative influence of the chain and the condensed groups.

CONTENTS

I. INTRODUCTION

The identification of hydrocarbons by other than physical properties is difficult because of their inertness to chemical reactions which might serve as tests. Furthermore, identification by physical properties requires a high degree of purity of the sample and accurate data on compounds of known structure for comparison. The study of the properties of the crystals offers a possible means of identifying the chief constituents of a mixture without actually isolating the materials. A number of experimenters have studied the crystal behavior of hydrocarbon waxes,[4 5] and some observations have been made on lower-melting hydrocarbons.[6 7] In this work an attempt has been made to obtain a series of photomicrographs of the crystals of the low-melting paraffinic, cycloparaffinic, and aromatic hydrocarbons for use in comparison with materials isolated from the naphtha fraction of petroleum and to correlate the crystal habit with molecular structure, if possible.

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[4] S. W. Ferris, A. C. Cowles, Jr., and L. M. Henderson, Ind. Eng. Chem. **23**, 681 (1931).

[5] G. D. Graves, Ind. Eng. Chem. **23**, 762 (1931).

[6] R. T. Leslie, J. Research NBS **15**, 41 (1935) RP808.

[7] R. T. Leslie, J. Research NBS **17**, 761 (1936) RP943.

While the difficulties in measuring extinction angles at low temperatures are not insuperable, some modification of the apparatus would be necessary, and this work is confined to the study of the appearances of the characteristic crystal forms.

II. APPARATUS AND METHOD

Figure 1 is a diagram of the apparatus used in securing the photographs. Its final form resulted from a number of attempts to build an apparatus which was convenient, economical, and rapid in operation. Some of the photographs shown in a previous work by the author were made by C. P. Saylor in an apparatus designed for observing crystals of rubber.[8] The chief differences are in the placing of the microscope objective within the cold chamber, the somewhat more compact cooling unit, and the side opening in the vacuum chamber for ease in manipulation of the sample. A microscope suitable for work at low temperatures has also been described by S. Erk,[9] which involves the use of a cooling unit submerged in a Dewar tube in place of the ordinary microscope stage. The experience of the present authors indicates that difficulty would be encountered with frost in such an arrangement during the time necessary to grow crystals of hydrocarbons.

The diagram of the apparatus is self-explanatory, and only a few details of construction will be emphasized. With some microscope objectives it was found that the low temperatures affected the canada balsam and caused the lenses to separate. Such lenses could be restored to usefulness by clamping them together and warming in an oven. Satisfactory lenses which will not split with large temperature changes are obtainable from some manufacturers, however. A 10× objective with a camera arrangement equivalent to a 10× ocular giving a magnification of about 100 times was used in this work. The bottoms of the vacuum jacket through which the illumination passed were made by sealing in disks of optically polished glass. It was found that simple flattening of the bottoms and polishing on the outsides before making the seal at the top of the dewar tube, leaving the inside unpolished, gave surfaces which distorted the light beam and produced nonuniformly illuminated fields. The evacuated tube in the barrel of the microscope was made by placing polished glass disks on the ends of the tube, heating in an electric furnace almost to their softening temperature, and sealing with a tiny gas flame while still in the furnace (Fairchild furnace method).[10] A practically undistorted surface was obtained by this means. The Polaroid screen (iodoquinine sulphate crystals on cellulose acetate) was found to be effective as a polarizing agent. The glass "stage", *R*, was a polished disk of such a diameter that it could be removed from the apparatus through the side tube, *P*. A variable resistance was placed in series with the Photoflood light, C_1, and it was burned at full capacity only during the exposure of the plates. With the single light it was found that exposures of 1 or 2 minutes were required for "process panchromatic" plates. Only 3 to 20 seconds were required for "superpanchromatic" plates, and most of the photographs were made with the latter. The cryostat was made from a single rod of brass, by boring out the center, turning recesses

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[8] W. H. Smith, C. P. Saylor, and H. J. Wing, B.S J. Research **10**, 479 (1933) RP544.

[9] S. Erk, Physik Z. **36**, 451 (1935).

[10] C. O. Fairchild, J. Opt. Soc. Am. **4**, 496 (1920).

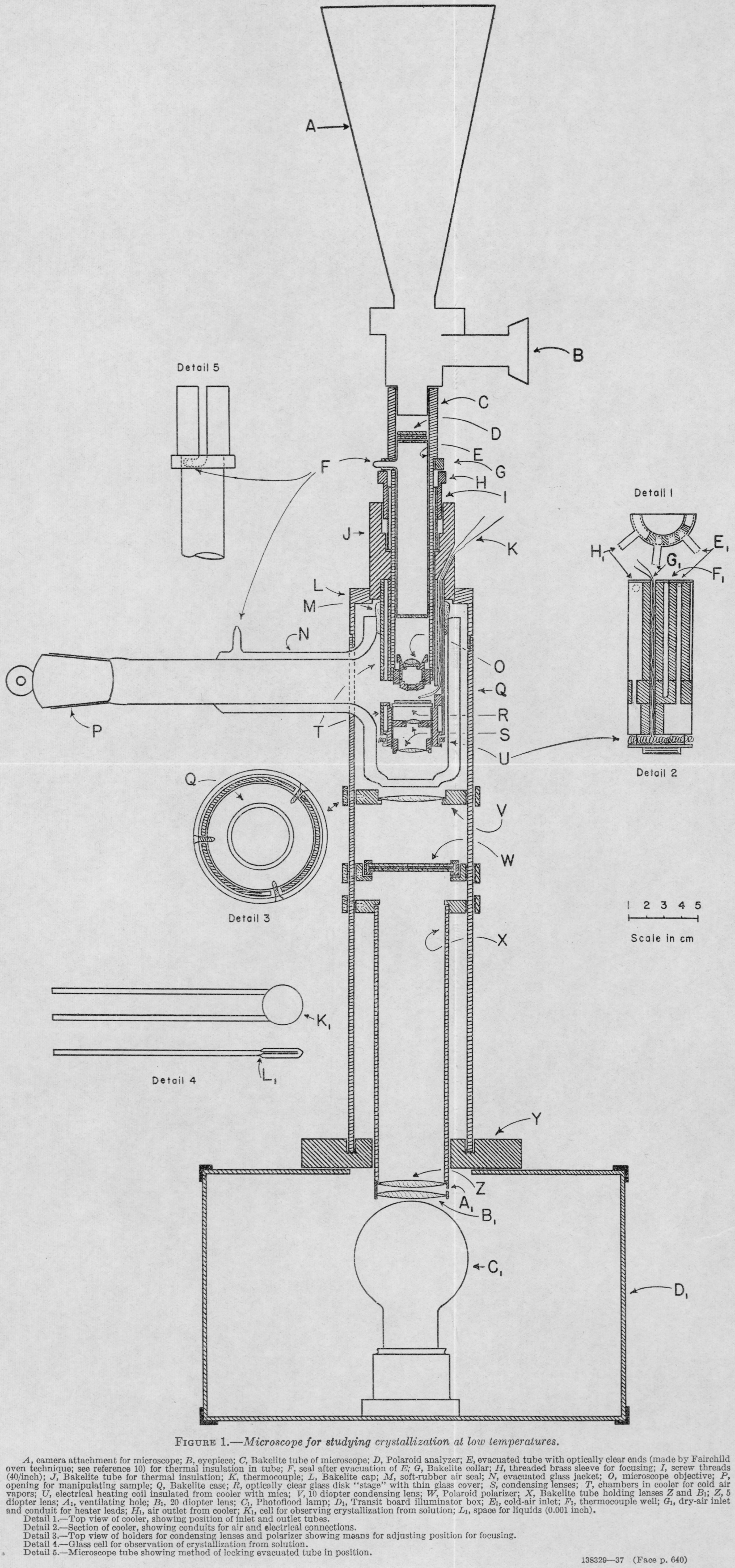

FIGURE 1.—*Microscope for studying crystallization at low temperatures.*

A, camera attachment for microscope; *B*, eyepiece; *C*, Bakelite tube of microscope; *D*, Polaroid analyzer; *E*, evacuated tube with optically clear ends (made by Fairchild oven technique; see reference 10) for thermal insulation in tube; *F*, seal after evacuation of *E*; *G*, Bakelite collar; *H*, threaded brass sleeve for focusing; *I*, screw threads (40/inch); *J*, Bakelite tube for thermal insulation; *K*, thermocouple; *L*, Bakelite cap; *M*, soft-rubber air seal; *N*, evacuated glass jacket; *O*, microscope objective; *P*, opening for manipulating sample; *Q*, Bakelite case; *R*, optically clear glass disk "stage" with thin glass cover; *S*, condensing lenses; *T*, chambers in cooler for cold air vapors; *U*, electrical heating coil insulated from cooler with mica; *V*, 10 diopter condensing lens; *W*, Polaroid polarizer; *X*, Bakelite tube holding lenses *Z* and B_1; *Z*, 5 diopter lens; A_1, ventilating hole; B_1, 20 diopter lens; C_1, Photoflood lamp; D_1, Transit board illuminator box; E_1, cold-air inlet; F_1, thermocouple well; G_1, dry-air inlet and conduit for heater leads; H_1, air outlet from cooler; K_1, cell for observing crystallization from solution; L_1, space for liquids (0.001 inch).

Detail 1.—Top view of cooler, showing position of inlet and outlet tubes.

Detail 2.—Section of cooler, showing conduits for air and electrical connections.

Detail 3.—Top view of holders for condensing lenses and polarizer showing means for adjusting position for focusing.

Detail 4.—Glass cell for observation of crystallization from solution.

Detail 5.—Microscope tube showing method of locking evacuated tube in position.

for the liquid air chambers, hard-soldering in blocks of brass into which the various channels for air, etc., were milled, and soft-soldering the jacket over the outside. It was found necessary to allow at least half a centimeter between each channel in order to be sure of a seal between them. The glass cells shown in detail 4 were made by spacing the polished disks with platinum foil or steel ribbon of the desired thickness and sealing most of the circumference of the beveled edges. The spacing ribbon was then withdrawn and the side tubes joined. Cells of 0.01 and 0.001 inch were tried. For most hydrocarbons, however, the cells were found impractical because of the necessity for seeding and otherwise manipulating the samples to produce cyrstal growth. A positive pressure of dry air was maintained within the apparatus by attaching a poorly evacuated dewar tube containing boiling liquid air to G_1. The liquid air for cooling was drawn into the apparatus by suction at H_1, and the temperature was controlled by varying the suction and the current through the heating coil, U.

A great deal of experience was required to grow crystals which were satisfactory for study, and the hydrocarbons differed greatly in the ease with which they formed large easily observable crystals. As much as 3 or 4 hours of patient warming and cooling was required for many of the crystals. Prolonged observation was also necessary in many cases to determine the characteristic behavior, since the crystals sometimes grow in anomalous and misleading forms. Repeated crystallizations generally make the distinguishing crystal forms obvious. No rigorous procedure can be described which will insure satisfactory results but the following are two of the methods which were found useful.

1. CRYSTALLIZATION WITHOUT SOLVENTS

Hydrocarbons which crystallized readily (generally above −100° C) were observed by introducing a very small amount into the stage with an "eyedropper" drawn out to a very long capillary. The material was introduced after the apparatus had almost reached the freezing temperature, to avoid evaporation and condensation on the lenses. The first crystals generally appeared as masses of small size. The apparatus was then allowed to warm very gradually until most of the mass was melted, and the few remaining crystals formed nuclei for the growth of better formed ones on second cooling. The thin glass cover on the stage shown in the figure aided in obtaining a field with little depth which could be focused readily, but it was not necessary and sometimes interfered with crystal growth. If great undercooling occurred, it was found that crystallization could be induced by touching the edge of the stage with a chilled glass rod or introducing a few seed crystals from a mass which had been formed outside the instrument, from solvents if necessary.

2. CRYSTALLIZATION WITH SOLVENTS

Materials which form glasses or poorly developed crystals could generally be crystallized from solvents outside the apparatus, some of the crystals being then transferred to the stage with a little of the solvent by drawing them up into a glass tube of about 1-mm bore and discharging them by forcing a small glass rod down the tube. This procedure prevented the formation of much ice in the transfer.

The crystals were then improved by alternate warming and cooling, as described above. For the photographs shown in this work, small quantities of the hydrocarbons in propane were poured into a few milliliters of liquid methane. When this procedure is followed, the electric heater should not be used, because of the danger of igniting the gases.

III. DISCUSSION OF CRYSTAL BEHAVIOR

The photomicrographs have been grouped according to type and homologous series as much as possible. Thus from the upper-left cut of figure 2 to the upper-left view of figure 5, inclusive, are crystals of aromatic hydrocarbons; from the upper left of figure 5 to the middle left of figure 6 are cycloparaffins; from the middle right of figure 6 to the upper left of figure 9 are normal paraffins; and from the upper-right cut of figure 9 through figure 10 are branched-chain paraffins. More than one photograph of some of the compounds are shown to give an idea of the different appearance which the crystals may be expected to present. Because of interference patterns most of the crystals produced highly colored kaleidoscopic effects. All except cyclohexane were visible between crossed polarizing screens, indicating that they were birefringent (transmitted light at different velocities along different axes). Cyclohexane crystals, which have cubic structure, were only slightly birefringent and were nearly invisible with polarized light. They also showed no pronounced symmetry of crystal appearance with unpolarized light, though the material had other characteristics of a very pure, easily crystallized substance (white appearance and good cooling curve). The round, pebble-like grains which were photographed were obtained only after careful growth, the tendency being to form masses of very tiny crystals.

The aromatic hydrocarbons, with the exception of ethylbenzene, formed crystals, highly colored under polarized light, which grew rather easily. The cycloparaffins, except cyclohexane, were also readily crystallized, though they generally require seeding and some manipulation to cause them to grow. It is to be noted that the crystals of the aromatic and the corresponding cycloparaffins bear no resemblances. The normal paraffins tended to crystallize readily as masses in most cases, and dilution with solvent was necessary to form single crystals which could be studied. They crystallized readily in most cases. The branched-chain hydrocarbons were more difficult to crystallize. All of these crystals were obtained from solvents. *n*-Pentane, 2-methylbutane, and methylcyclopentane were particularly difficult to crystallize. They appeared to have less tendency to orient in individual crystal units than the other materials. No very good photographs of these substances were obtained, partly because of lack of time.

Examination of the normal hydrocarbons shows that they tend to form long prismatic crystals, while the hydrocarbons with closed chains, such as benzene, toluene, methylcyclohexane, etc., form more nearly equidimensional polyhedrons. With increasing number and length of the side chains on the rings, there seems to be an increased

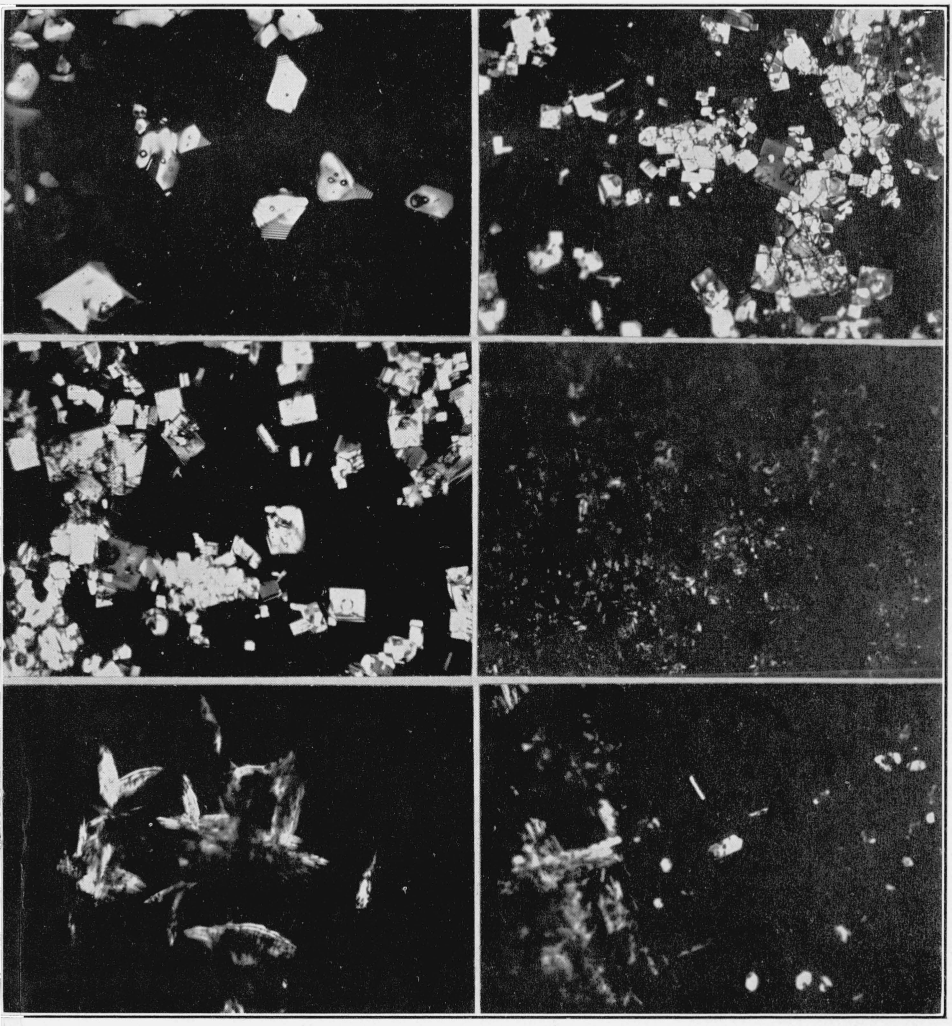

FIGURE 2.—*Crystals of aromatic hydrocarbons, benzene, toluene, ethylbenzene, and o-xylene.*

Upper left, benzene crystals (fp −5.5° C) grown from a solution containing a small quantity of petroleum distillate (bp 117 to 118° C, no freezing point); upper right, toluene (fp −95° C) crystallized by dilution as with benzene; middle left, toluene crystallized by dilution with a mixture of the petroleum hydrocarbon and propane; middle right, ethylbenzene (fp −92° C) crystallized from a solution of propane, showing very fine crystals which appeared first before growth; lower left, ethylbenzene crystallized from propane and grown by warming almost to the melting point and cooling slowly; lower right, *o*-xylene (fp −25° C) crystallized from solution in petroleum ether.

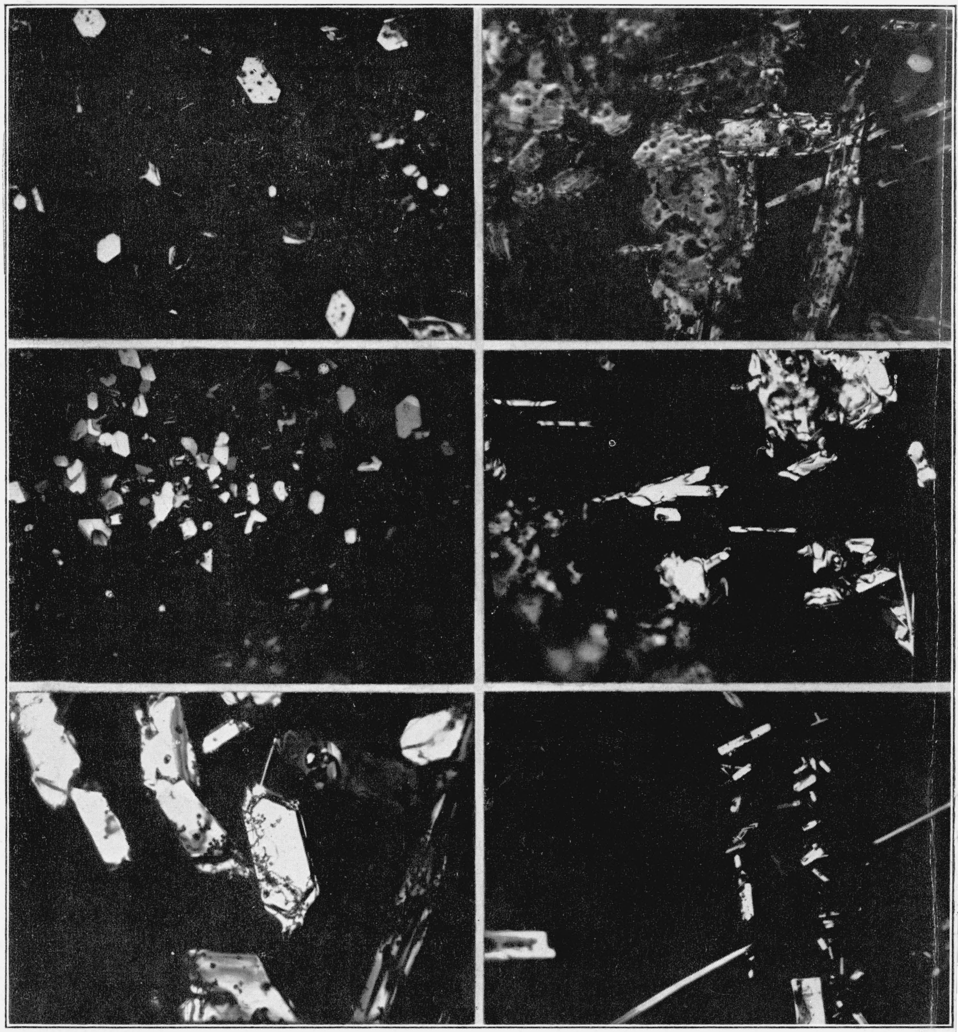

FIGURE 3.—*Crystals of aromatic hydrocarbons, o- and m-xylene.*

Upper left, *o*-xylene crystallized from petroleum ether; upper right, *m*-xylene crystallized alone, showing masses of crystals with frost present; middle left, *m*-xylene crystallized from petroleum ether, some of the crystals bearing resemblances to those of benzene; middle right, *m*-xylene crystallized from propane; lower left, *m*-xylene crystallized from propane and crystals grown; lower right, *p*-xylene (fp −13° C) crystallized from propane.

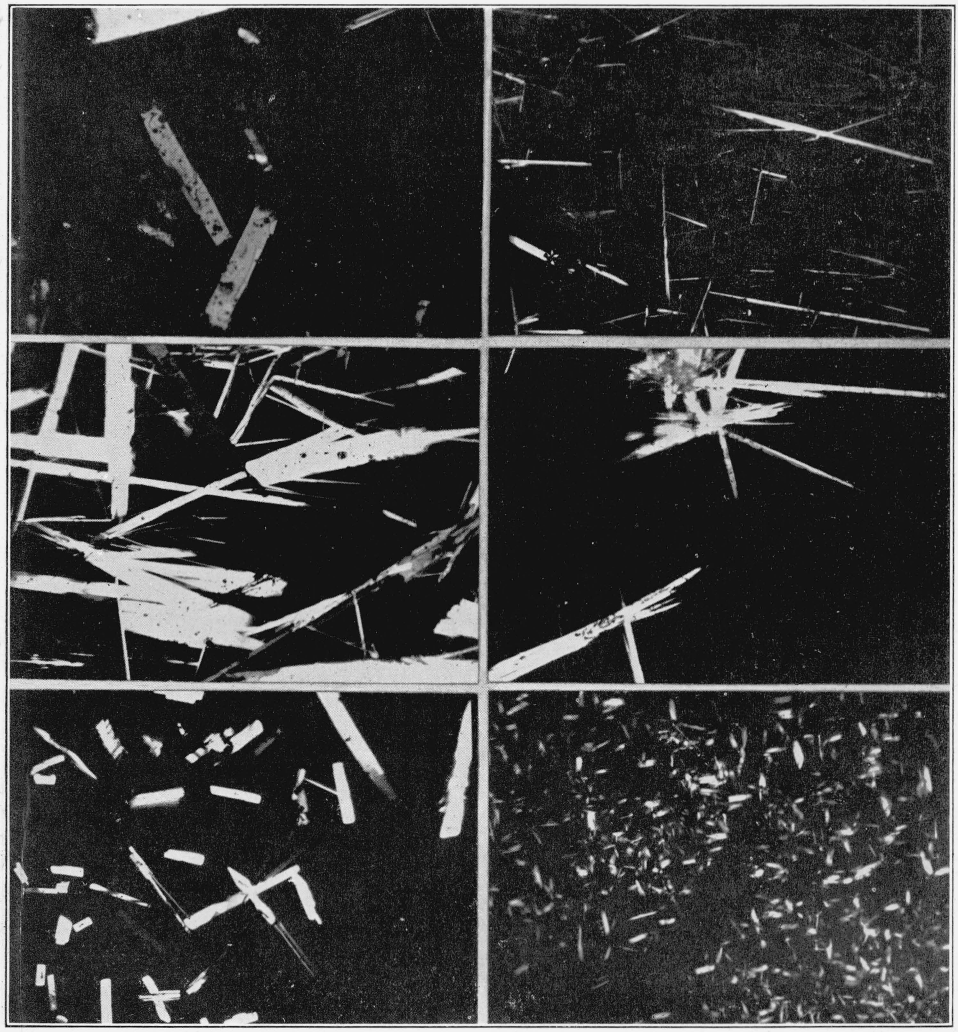

FIGURE 4.—*Crystals of aromatic hydrocarbons, p-xylene, mesitylene, hemimellitene, pseudocumene.*

Upper left, *p*-xylene crystallized from propane and crystals grown; upper right, mesitylene (fp −44.8° C) crystallized from mixture of petroleum and propane (see toluene), showing fine crystals which appeared on cooling without seeding; middle left, mesitylene crystallized from petroleum and propane, showing coarse crystals which appeared on continued cooling; middle right, mesitylene from petroleum and propane, showing coarse crystals which remain after warming; lower left, hemimellitene (fp −25.4° C) crystallized from petroleum distillate (bp 117 to 118° C); lower right, pseudocumene (fp −45° C) with petroleum distillate and propane.

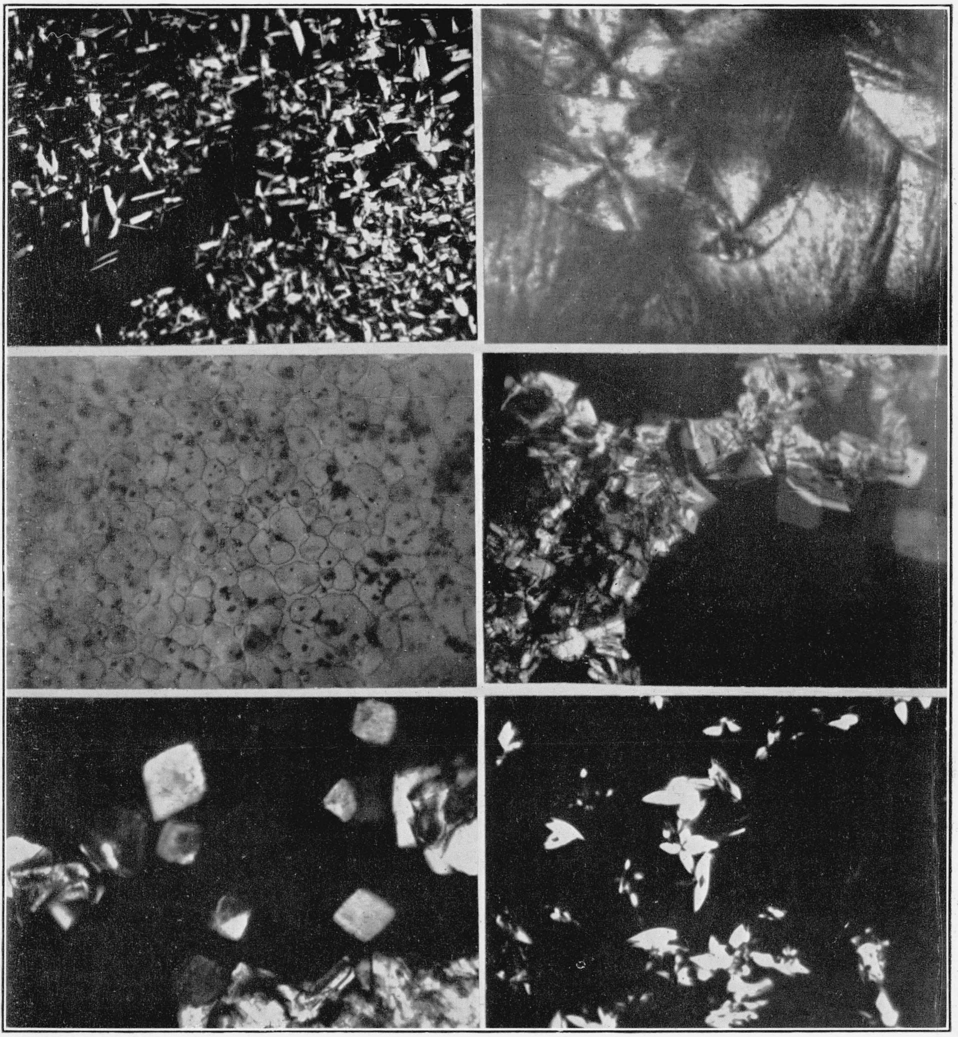

FIGURE 5.—*Crystals of aromatic and cycloparaffinic hydrocarbons, pseudocumene, methylcyclopentane, cyclohexane, methylcyclohexane, and ethylcyclohexane.*

Upper left, pseudocumene, second view; upper right, methylcyclopentane (fp −141° C) crystallized with methane and propane as solvents; middle left cyclohexane (fp −6.4° C) crystallized from petroleum distillate and viewed with unpolarized light; middle right, methylcyclohexane (fp −126.4° C) crystallized from solution in methane and propane; lower left, methylcyclohexane, second view; lower right, ethylcyclohexane (fp −111.4° C) crystallized from solution in methane and propane.

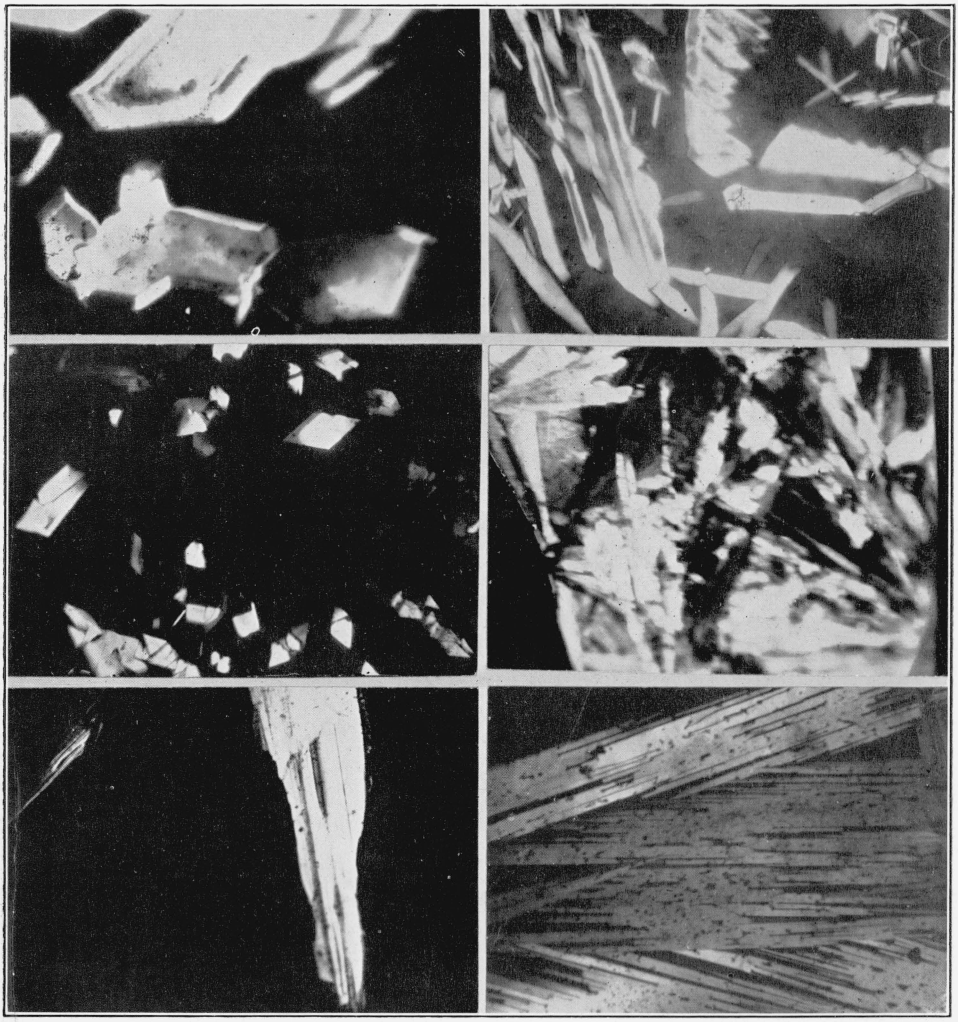

FIGURE 6.—*Crystals of cycloparaffinic and normal hydrocarbons, ethylcyclohexane, m- and p-dimethylcyclohexane, n-pentane, and n-hexane.*

Upper left, crystals of ethylcyclohexane grown by warming and refreezing; upper right, *m*-dimethylcyclohexane (fp −79° C) seeded with crystals grown from solution in propane; middle left, *p*-dimethylcyclohexane (fp −37° C) from solution in propane; middle right, *n*-pentane (fp −129° C) crystallized without solvent showing masses which appear after undercooling; lower left, *n*-pentane showing crystals formed after careful growth; lower right, *n*-hexane (fp −95° C) crystallized without solvent showing parts of large crystals.

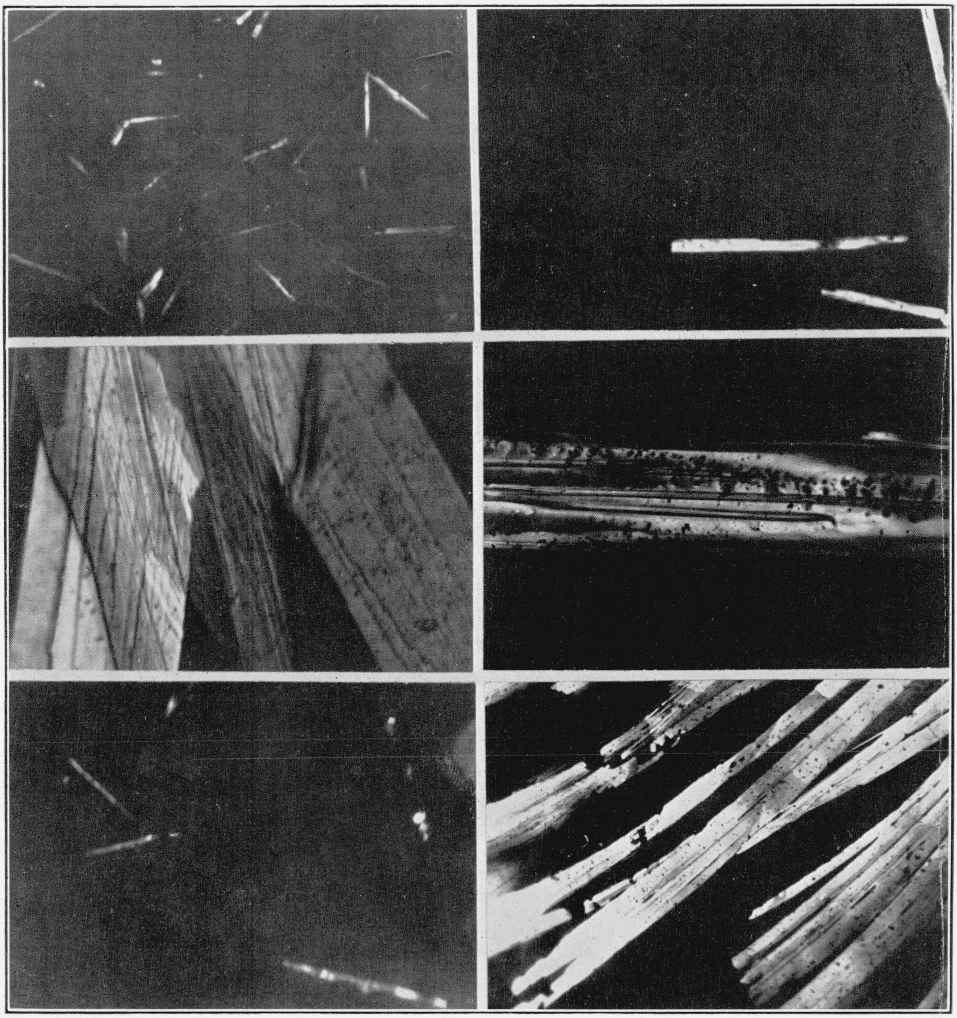

FIGURE 7.—*Crystals of normal hydrocarbons, n-hexane to n-nonane.*

Upper left, *n*-hexane crystallized from propane, showing smaller crystals; upper right, *n*-heptane (fp −90° C) crystallized from solution in propane; middle left, *n*-octane (fp −56° C) frozen without solvent, showing parts of large crystals; middle right, *n*-octane without solvent; lower left, *n*-octane crystallized from propane; lower right, *n*-nonane (fp −53° C) crystallized without solvent.

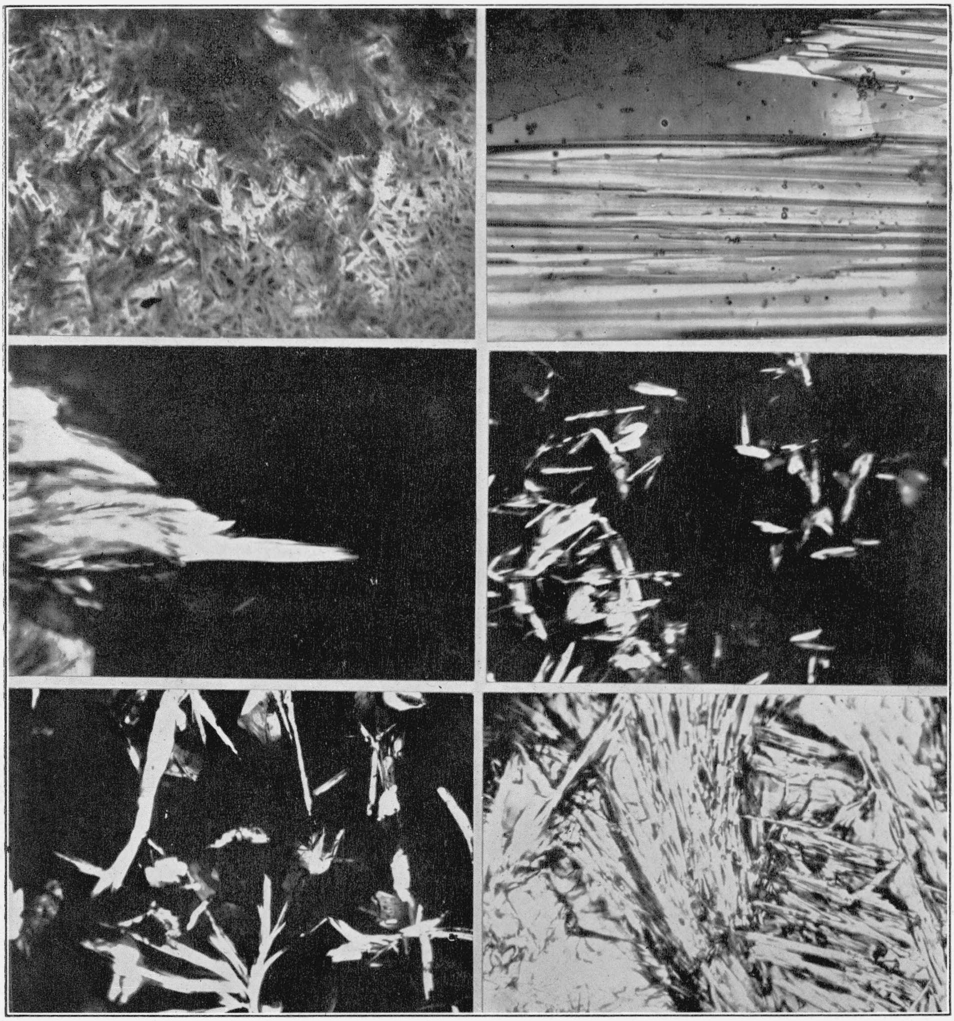

FIGURE 8.—*Crystals of normal hydrocarbons, n-decane to n-dodecane.*

Upper left, *n*-decane (fp −29° C) without solvent, showing masses of crystals resulting from undercooling; upper right, *n*-decane without solvent, showing large crystals; middle left, *n*-undecane (fp −25° C) without solvent, showing massive growth; middle right, *n*-undecane without solvent (this sample was difficult to grow in regular crystals); lower left, *n*-undecane without solvent, showing small crystals; lower right, *n*-dodecane (fp −10° C), showing masses of crystals.

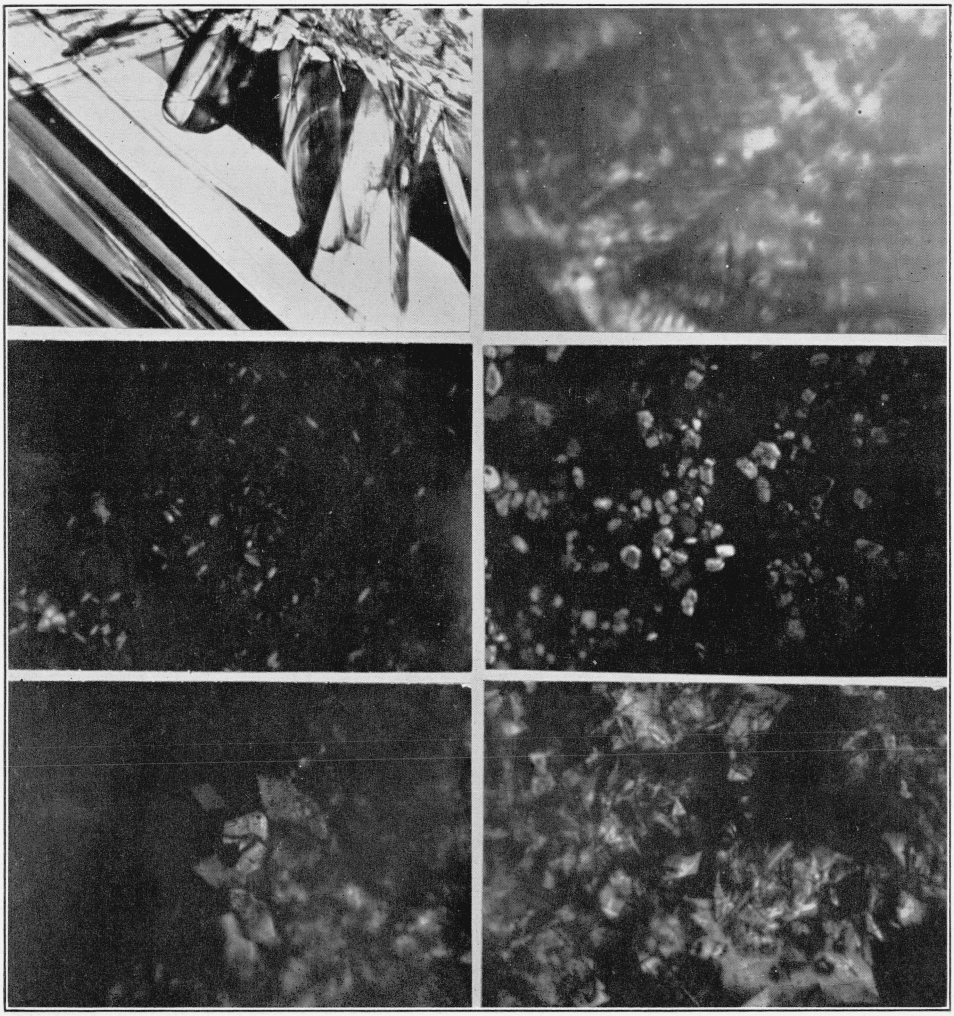

FIGURE 9.—*Crystals of normal and branched-chain hydrocarbons, n-dodecane, 2-methylbutane, 2,4-dimethylpentane, and 2,2,4-trimethylpentane.*

Upper left, *n*-dodecane showing large, isolated crystals; upper right, 2-methylbutane (fp −159° C) crystallized from methane and propane and transferred to the microscope (no single crystals are visible); middle left, 2-methylbutane crystallized from methane and propane, showing small crystals; middle right, 2,4-dimethylpentane (fp −119° C) crystallized from methane and propane, showing small crystals of about equidimensional section; lower left, 2,2,4-trimethylpentane (fp −107° C) crystallized from methane and propane, showing the typical crystals of quadrilateral section; lower right, 2,2,4-trimethylpentane, second view.

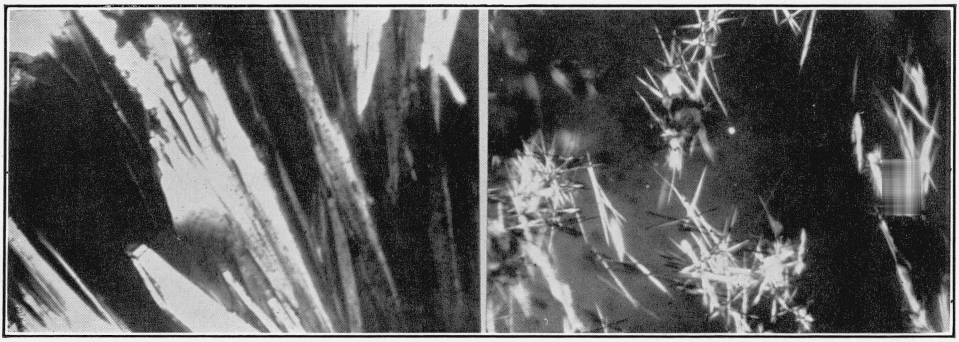

FIGURE 10.—*Crystals of branched-chain hydrocarbons, 2,2,5-trimethylhexane and 2-methylheptane.*

Left, 2,2,5-trimethylhexane (fp −106° C) crystallized from methane and propane, showing crystals which resemble those of normal hydrocarbons; right, 2-methylheptane (fp −111° C) crystallized from methane and propane, showing small prisms.

tendency to crystallize in the long forms of the normal paraffins; cf. dimethyl- and trimethylbenzene and the corresponding cycloparaffins. Examination of the highly branched paraffins with short chains (condensed molecules) shows that they also tend to crystallize in equidimensional polyhedrons, cf. isopentane, 2,4-dimethylpentane and 2,2,4-trimethylpentane, while the hydrocarbons with longer chains and fewer branches, such as 2,2,5-trimethylhexane and 2-methylheptane, resemble the normal compounds in their tendencies to the long flat shapes.

The crystals of mesitylene are interesting because they are known to undergo a transition in form, and the sample used for this work showed an anomalous behavior of the freezing curve. When cooled after fresh distillation the freezing began at −51.7°, whereas, if freezing was induced by plunging a chilled rod into the material, the freezing halt occurred at about −44.7.[11] Once crystals of the higher-melting form had been induced, they reappeared on refreezing unless the sample was redistilled. It is possible that the upper-right and the middle cuts of figure 4 show what occur. The needle-like crystals of the upper-right cut occur on gradual cooling without seeding, whereas if crystallization is induced by a cooled rod, the lath-like crystals of the middle-left cut appear. Warming the material causes the needle-like crystals to melt before the lath-like ones, as shown by the middle-right cut, indicating that the latter were stable at higher temperatures than the former ones.

Examination of the photographs of paraffin waxes shown by Ferris, Cowles, and Henderson [12] shows quadrilateral shapes somewhat similar to methylcyclohexane, 2,2,4-trimethylpentane and hydrogenated *p*-xylene, whereas the elongated six-sided crystals are similar to *m*-xylene. The more nearly equilateral hexagons shown by these investigators resemble none of the crystals of the hydrocarbons examined in this work, but resemble those of an unidentified hydrocarbon isolated by the author from a fraction of petroleum distilling between 119 and 120° C.[13]

IV. CONCLUSIONS

From the study of a number of hydrocarbons of known structure it is concluded that the behavior on crystallization depends somewhat on the nature of the molecule, condensed molecules tending to form nearly equidimensional polyhedrons, while open chains form elongated prisms. Mixed molecules (molecules in which chains are attached to groups with condensed structure) show modified forms depending on the relative influence of the chains and the condensed groups.

Successive members of the homologous series of the normal paraffins can not be distinguished by the appearance of their crystals, and hydrocarbons of different types but probably of the same classifications (condensed or open structure) may bear considerable superficial resemblance as, for example, methylcyclohexane and 2,2,4-trimethylpentane.

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[11] B. J. Mair, BS J. Research **11**, 665 (1933) RP614.
[12] Ind. Eng. Chem. **23**, 681, (1931).
[13] R. T. Leslie, J. Research NBS **15**, 41 (1935) RP808.

Hydrocarbons differ considerably in the ease with which their crystals tend to grow. The normal paraffinic and aromatic hydrocarbons grow more readily than the cycloparaffins or the hydrocarbons with branched open chains. The low-freezing pentanes and their derivatives do not grow readily.

Crystal behavior can be used in conjunction with other physical properties to identify the chief constituents in mixtures of hydrocarbons.

The authors are much indebted to C. P. Saylor of this Bureau for his technical advice and assistance in this work.

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