VOL. XXXIX. AUGUST, 1917. No. 8.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTE OF WASHINGTON.]

THE CRYSTALLIZATION OF MENTHOL.

BY FRED. E. WRIGHT.

Received March 19, 1917.

In physical chemistry the changes in the equilibrium relations between the different states, crystalline, liquid, and vapor, of a chemical compound with change in pressure and temperature, have been studied in great detail and are of extreme theoretical and practical importance. Experience has proved that with any given substance the phenomena resulting on such changes are not all equally well shown and that certain of the phenomena, as the lower melting temperature of an unstable form can be ascertained only with relatively few compounds. Of such compounds menthol exhibits apparently a greater variety of crystallization and melting phenomena than any other substance thus far examined by the writer. Menthol crystallizes in at least four different forms, α, β, γ, δ, only one of which, the α-form, is stable between zero and its melting temperature, 42.5°. The other three forms are monotropic and have lower melting temperatures, namely, 35.5° (β), 33.5° (γ), 31.5° (δ), respectively; all unstable forms invert finally into the stable α-form on standing; the δ-form may invert first into the β- and then into the α-form. At a given temperature the rate of growth of crystals of a given form from the undercooled melt is constant; also the rate of growth on inversion of an unstable form into one more stable. The tendency both on inversion and on crystallization from the melt is to form radial spherulites. These phenomena are so clearly marked and so readily observed on menthol that they merit brief description.

Optical and Crystallographic Properties.

The Stable α-Form.—For the experiments commercially pure menthol was used. Several different lots were tested and found to give essentially the same results. The crystals are prismatic in form but are without measurable end-terminations; the ends are commonly rounded. The prisms range in length from a few tenths mm. to several cm. Three of the best developed prisms were measured on the goniometer; although the reflection signals from the faces were not of good quality because of prismatic striations, yet the angles obtained prove definitely that the crystal system is hexagonal[1] and that the first and second order prisms are present. The crystals cleave well after one of the prisms. The refractive indices were measured in sodium light by the immersion method in dilute Thoulet solution; $\epsilon = 1.476 \pm 0.001$, $\omega = 1.497 \pm 0.001$. The refractive indices were also measured on other material by Dr. H. E. Merwin of this laboratory and the values obtained: $\omega = 1.496$, $\epsilon = 1.474$. The agreement between the two sets of values is satisfactory. The birefringence was measured by means of the isochromatic rings in the interference figure on a plate normal to the optic axis and of measured thickness. The result was obtained, $\omega - \epsilon = 0.022$, agrees with the difference between the two measured refractive indices.

The crystals are uniaxial, and optically negative. Interference figures from the long, thin prisms were obtained by fitting the crystal into a vertical hole of proper size in a piece of cork, filing the protruding ends of the crystal down flush with the top and bottom surfaces of the cork, and covering each end with a drop of glycerine and a cover glass; observations were made with condenser removed and with low power (E. F. = 32 mm.) objective. The angular rotation in circular degrees was found to be in sodium light:

Length of prism in 1 mm.	22.5	11.6	5.0
Angular rotation	+56°	+29°	+13°

The rotation per millimeter length of prism is about 2.5° for the D-line. Rough measurements of the angular rotation per mm. for different wave lengths were made with a monochromatic illuminator as spectral source:

Wave length in $\mu\mu$	640	610	590	570	550	530
Angular rotation for plate mm. thick	2.0°	2.3°	2.5°	2.8°	3.1°	3.4°

These results prove that there is appreciable rotational dispersion with wave length and that the rotation is greater for blue rays than for red rays.

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[1] Des Cloiseaux, *Compt. rend.*, **70**, 1211–1212 (1870).

The refractive index of melted menthol at 25° is approximately 1.458 for sodium light. Melted menthol exhibits rotatory polarization but the direction of rotation is counterclockwise (laevorotatory) and therefore opposite to that of the crystals. $[\alpha]_D^{15°}$ of melted menthol as determined by Oppenheim[1] is —59.6°. This corresponds to a laevorotation of —0.53° per mm. depth of liquid. Measurements in sodium light by the writer showed at about 45° a laevorotation of —0.45° per mm. depth of liquid. The crystals are therefore not only rotatory in the opposite sense but their rotatory power is over 5 times as great.

The γ-Form.—This form crystallizes in sharply defined radial spherulites. Optically the fibers show negative elongation. The birefringence is approximately 0.006 or about $^1/_4$ that of the α-form. The interference colors for a slide of ordinary thickness are the bright colors of the first and second orders. The refractive indices could not be satisfactorily measured because of the rapidity with which this form inverts into the α-form. On inversion the preparation becomes filled with minute bubbles thus indicating a relatively large decrease in specific volume on passage into the α-form.

The β-Form.—Crystallizes also in radial spherulites which on standing invert into the α-form. Birefringence very weak between 0.001 and 0.002, about $^1/_4$ that of the γ-form; the interference colors even in thick sections do not exceed yellow of the first order and are usually first order grays. The average refractive index was measured directly on the total refractometer and found to be approximately 1.486. On standing the average refractive was observed to rise gradually to 1.489 as a result of the inversion into the more strongly refracting α-form. The elongation of the fibers is positive.

The δ-Form.—This form, which apparently has not been observed before, crystallizes in radial spherulites which are identical in general aspect with those of the β-form. The birefringence is also very weak between 0.001 and 0.002; but the elongation of the fibers is negative. This feature suffices to distinguish the two forms. The δ-form inverts, especially at low temperatures, rapidly into the β-form, which in turn changes into the α-form. The δ-form may, however, invert directly into the α-form, especially at higher temperatures. The specific volumes of the β- and δ-forms are evidently practically the same because on inversion there is no indication of a change in the light transmission qualities. The specific volume, moreover, of these forms and that of the melt cannot be very different because of the transparency of the radial spherulites.[2] This may

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[1] *Compt. rend.*, **53**, pp. 379, 483 (1861).

[2] Tammann, G., "Kristallizieren und Schmelzen," 40–41 (1903); Heydweiller, *Ann. Physik*, [3] **64**, 732 (1898).

be due in part to the very weak birefringence which has relatively little dispersive effect with overlapping fibers as compared with strongly birefracting fibers under the same conditions. On alteration into the β-form the inversion invariably begins at the center of the spherulite and proceeds outwards.

Melting Phenomena.

The α-Form.—The melting temperature of this form, 42.5°, was ascertained by two different methods. In the first the crystals were melted down between two strips of thin cover glass; the lower strip was clamped at one end to a thin brass rod or fused to a thin glass rod which served as handle to immerse the slide in a beaker of water placed on the microscope stage and kept at a definite temperature by means of a small electric resistance heating coil of fine, enamelled constantan wire. On plunging the slide into the water the melting phenomena were observed in polarized light. This method insured a rapid and sufficiently exact determination, within 0.5° of the temperature which was read off on a mercurial thermometer in the stirred water. In the second method a thermoelement of thin wires of constantan (0.05 mm. diameter) and of copper (0.015 mm. diameter) were used; temperatures were read off by means of a direct-reading millivoltmeter with an accuracy of about 0.25°. The hot junction of the thermoelement was placed in the menthol melted between either an object glass and a cover glass or between two strips of cover glass. These were placed either on a plate of copper with a transverse hole drilled to allow passage of light or in a specially constructed electric resistance heater which is wound with fine therlo wire (No. 36) and which rests on the microscope stage; into this heater the object glass is inserted. The heater is used with resistance in series on a 110 volt circuit; with it temperatures up to 100° can be had. It is insulated with mica and asbestos and is covered with thin copper sheeting. It is simple in construction and has proved satisfactory in use.

Melted menthol shows undercooling to a pronounced degree and does not crystallize within reasonable time until after a temperature of 32° or lower has been reached. Crystals of the α-form grow at an appreciable rate of 42°. On crystallization from the melt at the higher temperature needles are commonly formed; these show a tendency toward radial arrangement. At lower temperatures radial spherulites are almost invariably formed and the fibers do not grow out as separately distinguishable individuals but as fibrous, radial aggregates. These show optically negative elongation. Other phenomena of crystallization are noted in a separate section below.

The β-Form.—Determinations of the melting temperatures of this form and of the two other monotropic forms were made by the methods described above. Such measurements are possible because of the high degree of undercooling of the α-form and its slow rate of crystallization from the melt at temperatures above 30°. The melting point of the β-form is approximately 35.5°.

The γ-form melts in the presence of both α- and β-forms at about 33.5°. At 34° it disappears completely; at this temperature the α- and β-forms fail to show a trace of melting.

The δ-Form.—This form is most conveniently obtained by placing a cover glass slide of melted menthol against a block of ice and cooling it rapidly to 0°. At this temperature radial spherulites of the δ- and also of the β-form flash out over the whole slide. If now the crystallized slide be plunged into water or glycerine heated to 32°, all of the δ-form is seen to disappear completely. At 31° it alters rapidly into needles of the α-form. Its melting temperature is approximately 31.5°.

In the case of any one of the three monotropic forms it is possible to melt a given form in the presence of other forms which have a higher melting temperature. Thus on heating a preparation containing all four forms to 32° the δ-phase melts down and disappears while the γ- and β-forms proceed to invert rapidly into the α-form. At 34° both the δ- and γ-forms disappear. At 36° the stable α-form alone remains and the crystals proceed to grow slowly.

These results prove the order of stability of the several monotropic forms. They illustrate in a convincing manner the well established theoretical conclusion that a monotropic form melts at a lower temperature than the stable form. This relation is easily realized experimentally in menthol because of the pronounced undercooling of its melt and relatively slow rate of crystallization of the stable form from the undercooled melt. The undercooled melt has been considered to be in a colloidal state by some observers, but it would seem to be difficult to picture such a state in the melt of a pure substance.

A simple experiment to prove the lower melting point of a monotropic form and one which can be projected from a polarization microscope on a screen is to melt down menthol between object glass and cover glass, to allow it to crystallize at room temperature (the growing crystals projected on the screen) and then to touch a part of the slide at which both the α- and γ-forms are present with a heated glass or metal rod. The γ-form melts down and disappears completely, leaving the α-form untouched and surrounded by the dark, isotropic background of the melt.

Inversion Phenomena.

The inversion phenomena of menthol have been studied by Dahms,[1]

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[1] *Ann. Physik,* [3] **54**, 486, 513 (1895).

Schaum,[1] Heydweiler,[2] Pope,[3] Oppenheim,[4] Arth,[5] Tammann,[6] and Hulett.[7] Their studies established the fact that there are at least three different phases of crystallized menthol and that two of these on standing change into the stable α-form. These relations are corroborated by the present investigation and in addition other relations have been observed which are recorded below.

Inversion of the γ-Form into the α-Form.—Several minutes after crystallization of the γ-form its incipient alteration into the α-form can be seen at different points in the section. The points most liable to be attacked first are the peripheries and the centers of the spherulites. Here and there the point of alteration may be located between the center and the margin of a spherulite. The replacing α-form crystallizes as a radial spherulite, or rather concentrically arranged, fan-shaped, groups grow from the margin toward the center. In all cases the rate of growth is for a given direction constant at constant temperature and increases with rise in temperature. At 22.5° the rate of growth, as measured by means of a coördinate micrometer eyepiece, of the α-form replacing a spherulite of the γ-form and growing from the center outwards is 0.027 mm. per minute (Table I).

TABLE I.

Time in minutes.	Position of outer edge along positive x-axis scale divisions.	Growth per minute in scale divisions.	Time in minutes.	Position of outer edge along positive x-axis scale divisions.	Growth per minute in scale divisions.
0	16		7	39	3.5
1	19	3	8	42.5	3.5
2	22.5	3.5	9	46	3.5
3	26	3.5	10	49.5	3.5
4	29	3.0	11	52.5	3.0
5	32	3	12	56	3.5
6	35.5	3.5	13	59	3.0

For the optical arrangement employed 1 scale division = 0.0082 mm. The average rate of growth is 3.3 scale divisions per minute or 0.027 mm. In case the crystallization begins at some point between the center and the margin the α-form still crystallizes out as a radial spherulite but the rate of growth transverse to the fiber direction (tangential) is greater than that along the fiber direction (radial) with the result that approximately an ellipse and not a circle in cross section results, the ratios of the major and minor axes ranging from 3 to 4 to 7 to 8 in the different spherulites measured. There is evidently a pronounced shrinkage in volume on alteration as the preparation becomes filled with bubbles and less transparent.

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[1] *Ann.*, **308**, 39 (1899).

[2] *Ann. Physik*, [3] **64**, 725, 733 (1898).

[3] *J. Chem. Soc.*, **75**, 463 (1899).

[4] *Compt. rend.*, 378 (1861); *Ann. chim. phys.*, **120**, 352 (1861).

[5] *Ann.*, [6] **7**, 438 (1886).

[6] "Kristallizieren und Schmelzen," 40–41 (1903).

[7] *J. Phys. Chem.*, **28**, 667 (1899).

The Alteration of the β-Form into the α-Form proceeds commonly from many points and its rate is not so readily measured. The whole radial spherulite, especially near the center, becomes dotted, shortly after crystallization, with specks of the α-form which gradually increase in size and finally replace the entire spherulite. At higher temperatures, above 28°, the α-form may appear in the form of separate needles which, on growing, cut across the spherulites in any direction. The tendency of the α-phase to form radial or fan-shaped aggregates is less pronounced at high temperatures than at low.

The Alteration of the δ-Form into the β-Form proceeds almost invariably from the center outwards. There is practically no volume change on alteration. The alteration takes place so uniformly that for a time it appeared as though the phenomena observed might be ascribed to rapid change in the shape of the optic ellipsoid of the β-form such that at low temperatures the α-axis is parallel with the elongation while at high temperatures this axis gradually increases in length until it equals and then becomes the γ-axis. This assumption was strengthened by an apparent rapid decrease in birefringence of the δ-form with increase in temperature; but careful study proved that there is an abrupt change of the δ-form into the β-form and not a gradual transition. The β-form with positive elongation grows out from the center and finally replaces the spherulite of the δ-form. On cooling, moreover, to —12° the β-form does not pass into the δ-form as it should were the phenomenon simply one of rapid change in birefringence with temperature. The δ-form is best obtained by chilling menthol melted between two cover glasses directly on ice or on a mixture of salt and ice.

The Inversion of the δ-Form into the α-Form is similar in every respect to that of the β-form into the α-form. At the higher temperatures the α-form crystallizes out as individual needles which transverse a radial spherulite in any direction.

Rate of Growth of Radial Spherulites from the Melt.

In the case of radial spherulites crystallizing out from this melt it has commonly been assumed that the rate of growth of a given form along a radius for a given temperature is constant, irrespective of the size of the radial spherulite. In case two growing spherulites meet, the line of their intersection should be a curve such that the difference between the distances to the two centers is constant; the curve which satisfies these conditions is a hyperbola. Measurements on the curves of intersection of two spherulites of sulfur were first made by Popoff,[1] who found that they were hyperbolas. Measurements on the intersection curves of both β and γ menthol were made by the writer and are listed in Table II. The coördinates of a number of points were determined by means of a coördinate

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[1] Tschermak's *Mineralogy Petrog. Mitt.*, **23**, 153–180 (1904).

eyepiece; the distance from the center of each spherulite was computed; the differences between these distances are listed in Table II.

TABLE II.

a.	*b.*	*x.*	*y.*	Diff.	*a.*	*b.*	*x.*	*y.*	Diff.
		November 3, 1916.					December 17, 1915.		
—14	+40	0	0	26	—28	+40	—19	0	26
..	..	—1	10	25.8	..	..	—20	10	26.6
..	..	—2.3	15	25.9	..	..	—21.6	20	26.3
..	..	—4	20	26	..	..	—24	30	26.0
..	..	—5.9	25	26	..	..	—27.2	40	26.2
..	..	—8	30	26	..	..	—30.3	50	26.9
..	..	—10.2	35	26			November 3, 1916.		
..	..	—12.2	40	25.7	+3	—57	0	0	54
..	..	—14.1	45	25.4	..	..	2.4	5	54.6
..	..	—16.5	50	25.4	..	..	7.8	10	54.5
		November 3, 1916.			..	..	15	15	54.3
—13	+15	0	0	2	..	..	23	20	54.2
..	..	—0.3	10	2.1			November 3, 1916.		
..	..	—1.2	20	2.5	8	—20.5	0	0	12.5
..	..	—2.0	30	2.5	..	..	2	10	13
..	..	—3.1	40	2.7	..	..	6	20	13.1
..	..	—4.3	50	2.8	..	..	10.5	30	13.7
					..	..	16.1	40	13.4

These measurements prove that the rate of growth at a given temperature is essentially constant and independent of the size of the radial spherulite. The slight deviations in the differences (Column 5 of Table II) between the radial distances are constant within the limits of observational error.

Temperature as a Controlling Factor in Determining the Phase which Crystallizes Out from the Undercooled Melt.

In the case of monotropic substances experience has shown that on crystallization from a melt the degree of superheating of the melt before cooling, the rate of cooling, and the temperature at which crystallization takes place, are important factors in determining the phase which crystallizes out. The results on the crystallization of menthol indicate that of these factors the third, namely, the temperature at which crystallization takes place, is the most important. In order that the second factor, rate of cooling, be eliminated or rather made the same in each experiment, a beaker of water or glycerine was heated to a definite temperature; the menthol, melted between two cover glass slips, was plunged into the heated liquid to the temperature of which it cooled rapidly. The results of the observations are listed in Table III.

These results indicate that there is a temperature range for each of the four forms; within this range it is the phase most likely to crystallize out. Thus between 42° and 30° the α-form may be expected to crystallize out rather than any of the other forms; between 30° and 18° the γ-form is most likely to occur; between 18° and 5° the β-form; below 5° to —12° the δ-form. The rate at which these different phases crystallize from solution differs markedly; thus the α-form, which has the least specific volume, crystallizes relatively slowly while at 0° the β- and δ-forms, whose specific volumes are not very different from that of the liquid crystallize out with great rapidity. In the case of the γ- and α-forms the temperature of the melt was found to be raised several degrees on crystallization. This was detected by means of the copper constantan thermoelement on a slide allowed to cool in air.

TABLE III.

Temperatures.	Phase to crystallize out.	Temperatures.	Phase to crystallize out.
32°	α-form only	14.5°	Many composite radial spherulites, α-form in center, β-form outside of γ-form.
29°	chiefly α-form; some γ-form	10.5°	chiefly β-form; some γ-form
26.5°	chiefly γ-form; some α-form	5.5°	chiefly β-form; some γ-form; some δ-form
23°	chiefly γ-form; some α-form	0°	some β-form; δ-form
18.2°	some γ-form as centers of spherulites of β-form	—10°	chiefly δ-form; some β-form

The Formation of Radial Spherulites.

The crystallization of the different forms of menthol either from the melt or on inversion is remarkable because of the pronounced tendency to produce radial spherulites. According to the commonly accepted view of crystallization, a particular crystal configuration (spacial grouping of the component atoms) replaces another because it is more stable under the existing conditions of temperature and pressure. The crystallization begins at isolated points in the preparation and proceeds to grow outwards from them. With some substances there is a strong tendency at certain temperatures for the growth to proceed from the point outwards radially in all directions and thus to produce radial spherulites. At other temperatures, as in α-menthol at temperatures above 35°, this tendency toward the formation of radial spherulites is subordinate to the tendency to grow in individual prisms and crystals. Commonly radial spherulites or irregular aggregates are indicative of relatively rapid crystallization, whereas individual crystals indicate slower growth. On forming from a melt radial spherulites may grow equally well in any direction and the spherulites are roughly spherical in shape; but a radial spherulite which develops on inversion from a substance already in the crystal state does not grow with equal speed in the different directions because of the differences in inertia of the atomic complex in the different directions. This is probably due in part to an actual difference in size and shape of the rearranging atomic groups. Whatever the fundamental cause, experiment shows that there is a measurable difference of rate of growth on inversion in the different directions in the altering crystal with the result that the spherulites are no longer round but are flattened ellipsoids. The application of X-ray analysis to inversion phenomena of this kind promises a deeper insight into the mechanics of inversion phenomena of this and other types.

Summary.

The crystallization of menthol is interesting not only to the crystallographer but also to the physical chemist. Menthol appears in four different forms, α, β, γ, δ; three of these bear apparently monotropic relations to the stable α-form. Because of pronounced undercooling the melting temperatures of all four forms can be realized and their mutual relations can be studied directly under the microscope. On crystallization all forms of menthol show a pronounced tendency to the development of radial spherulites; these are roughly spherical in shape in the case of crystallization from the melt, but noticeably ellipsoidal on inversion of one crystal form into a second. The four forms of menthol are readily distinguished under the petrographic microscope. α-Menthol shows dextrorotatory polarization while the melt is laevorotatory. In the formation of the different monotropic forms the initial temperature of crystallization appears to be the determinative factor.

WASHINGTON, D. C.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 109.]

THE THERMODYNAMIC CONSTANTS OF AMMONIA.

I. THE HEAT-CAPACITY OF LIQUID AMMONIA.

BY FREDERICK G. KEYES AND HENRY A. BABCOCK.

Received June 2, 1917.

1. Introduction.

Although liquid ammonia has been in use for many years as a practical refrigerating agent, its various physical constants have not been hitherto completely determined with any considerable degree of precision. The practical as well as the scientific importance of an accurate body of data relating to the physical properties of the substance is very considerable. Aside from the use of ammonia in the refrigerating art the Haber process of atmospheric nitrogen fixation requires data for the gas phase which at present are lacking. From a scientific point of view, on the other hand, ammonia is very similar to water having a high dielectric constant and quite general solvent properties, thus rendering a study of the physical properties of the liquid phase of especial interest. In fact as will be