

The walls of the test-tube or the object-glass, which exhibit the said colour-phenomena, have that same structure, but with this difference, that the globular, concentrically deposited spherulites have much smaller dimensions and lie much closer together. Each little spherulite has also a cross; this however, is not dark, but coloured with yellow and violet arms. The spherulite is also coloured in the alternate circle-quadrants.

This ensemble of small, coloured spherulites is the cause of the said brilliant colour-phenomena; they are quite analogous to those which are wont to appear in the case of liquid crystals and remain in existence for an indefinite period. Each of them exhibits one or generally two luminous points in the centre; they exhibit a strong circular polarisation and are left-handed. The whole appears between crossed nicols as a splendid variegated mozaic of coloured cellular parts. The size of each individual is 0.5—1 micron.

The acetate also exhibits something similar, but the spherulites are built more radial and the whole is not at all so distinct.

I hope to contribute more particulars as to these remarkable phytosterol-compounds shortly. I have mentioned them here merely to show the importance of this structure-form for the optical phenomena, observed in the anisotropic phases.

*Zaandam*, 14 November 1906.

**Chemistry.** — “*On irreversible phase-transitions in substances which may exhibit more than one liquid condition.*” By Dr. F. M. JAEGER. (Communicated by Prof. FRANCHIMONT).

(Communicated in the meeting of November 24, 1906).

§ 1. The fatty esters of *α-Phytosterol* from *Calabar-fat*, which the Phytosterol mostly occurring in the vegetable kingdom, and which has also been isolated from rye and wheat under the name of “sitosterol”, exhibit very remarkable properties in more than one respect.

In my previous communication, I alluded briefly to the colour phenomena and the spherulite-structure in the *propionate* and the *acetate*. In the latter I could not observe anisotropic liquid phases: in the former a doubly-refracting phase is discernible just before melting, but it lasts too short a time to allow the accurate measurement of the temperature-traject.

With the following four terms of the series, however, these phenomena are more distinct, and occur under conditions so favourable as

could hardly be realised up to the present in the other known substances. They also exhibit enormous phenomena of retardation in their diverse transitions and often a typical irreversibility thereof, of which I will now communicate some particulars.

## § 2. Thermometrical behaviour of the fatty $\alpha$ -phytosterol-esters.

*A.  $\alpha$ -Phytosterol-n.-Butyrate*, on very slowly raising the temperature, melts at  $89^{\circ}.5$  to a turbid, doubly-refracting liquid *A*, which at first is very viscous but rapidly becomes thinner and is converted, at  $90^{\circ}.6$ , into a clear isotropous fusion *L* of the consistency of glycerol.

On cooling the same carefully, the thermometer falls gradually while the isotropous liquid thickens more and more but remains quite clear. At  $80^{\circ}$  the whole mass crystallises all at once to small crystals *S* with so great a caloric effect that the thermometer goes up to  $85^{\circ}$ . There is no question now of anisotropous liquid phases at all. These two experiments may be repeated at will but always with the same result. As to the nature of the turbid phase, compare "micro-physical behaviour".

If the isotropous fusion is suddenly cooled in cold water, a bluish-grey coloration appears and a soft, doubly-refracting mass is obtained, which does not become crystalline until after a very long time.

*B.  $\alpha$ -Phytosterol-Isobutyrate*, when treated in the same manner, melts at  $101^{\circ}.4$  to a glycerol-like, turbid, doubly-refracting liquid *A*, which gradually assumes the consistency of paraffin-oil and is converted at about  $103^{\circ}.2$ , apparently continuously, into a clear fusion *L*.

If this is cooled, it certainly becomes gradually thicker but it still remains quite clear and isotropous.

At  $80^{\circ}.4$  it becomes turbid and doubly-refracting: this phase is identical with *A*, and it has the consistency of glycerol: at  $73^{\circ}$  it has become as thick as butter, and at  $66^{\circ}$  the thermometer can be moved only with difficulty, whilst it may now be drawn into sticky, doubly-refracting threads. At  $65^{\circ}$  the thermometer suddenly goes up to  $68^{\circ}.8$  and the mass crystallises in long, delicate needles *S*.

On rapid cooling of the fused mass, this is converted into a turbid, greasy looking, doubly-refracting mass, which crystallises but very slowly: no colour-phenomena occur.

*C.  $\alpha$ -Phytosterol-n.-Valerate* melts, when in the crystallised condition, at an *uncertain* temperature. At about  $48^{\circ}$ , the substance commences to soften visibly, at  $54^{\circ}$  its consistency is that of thick butter, at  $80^{\circ}$  it is somewhat thinner, at  $85^{\circ}$  it is actually liquid, but still turbid and doubly-refracting. *All these transformations proceed quite*

*continuously*. At about  $97.5^\circ$  the liquid is clear and isotropous; it has then the thickness of paraffin-oil.

If, however, the isotropous fused mass is cooled, the isotropous paraffin-oil-like liquid remains clear to about  $87.3^\circ$ , when a turbid doubly-refracting phase is formed. This, on further cooling, gradually becomes more viscous; at  $80^\circ$  it is as thick as butter, at  $66^\circ$  it can hardly be stirred, and may be drawn into threads. It may be cooled to the temperature of the room without solidifying. It remains in this condition for hours, but after 24 hours it has again become crystalline. The substance, therefore, has no determinable melting or solidifying point.

*D.  $\alpha$ -Phytosterol-Isorvalerate* behaves quite analogously to the *n*-valerate. Neither a definite melting point, nor a solidifying point can be observed. The mass softens at about  $45^\circ$ , is anisotropous thick-fluid at  $65^\circ$ , and becomes clear and isotropous at  $81^\circ$ .

On cooling to  $78.1^\circ$ , a beginning of turbidity is noticed, the liquid gradually becomes thicker and is converted at an uncertain temperature into a tenacious sticky, doubly-refracting mass, which after 24 hours has again solidified to a crystalline mass.

§ 3. The thermometrical behaviour of these remarkable substances is represented in the annexed schematic *p-t*-diagram, for the case of the *n*-butyrate and *isobutyrate*. The typical irreversibility of these phenomena is thus seen at once. Moreover in the case of the two valerates, the whole behaviour can be described only as a real, *gradual* transformation, solid  $\rightleftharpoons$  liquid with an intermediate realisation of an indefinite number of optically-anisotropous liquids.

§ 4. **The micro-physical behaviour of the fatty  $\alpha$ -phytosterol esters.** Perhaps, there are no substances known, which exhibit under the microscope the characteristic phenomena of anisotropous liquids in so beautiful and singular a manner as these esters; in this respect the *isobutyrate* and the *valerate* excel in particular. In the normal *butyrate*, the traject, where the liquid crystals are capable of existence is rather too small. For this reason, although the behaviour of the four substances differs in details, I will describe more particularly the behaviour of the *n*-valerate and as to the others, I will state occasionally in what respect they differ from the valerate. In consequence of the totally different circumstances which the microscopic method involves, nothing more is seen of the thermically observed peculiar irreversibility and even progression of the transformations. For the study of the nature of the diverse phase-transformations, the

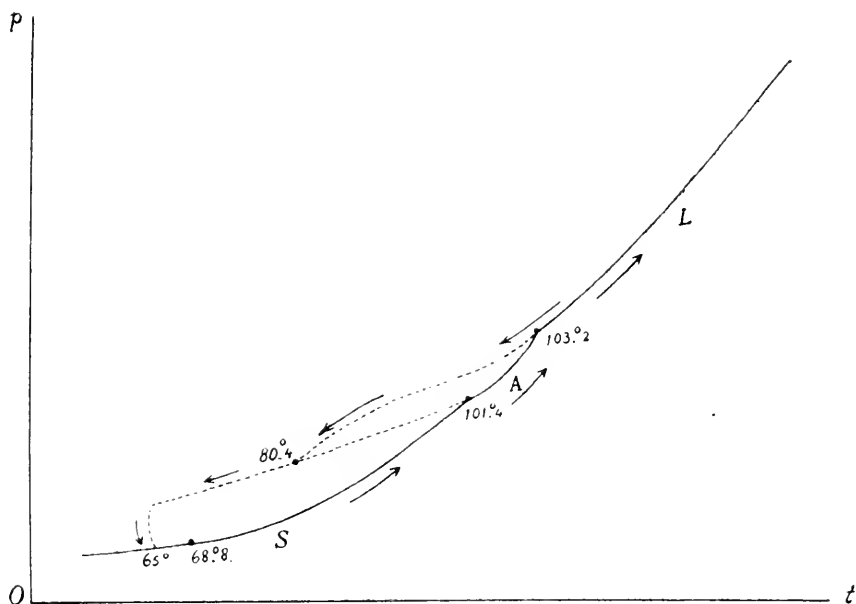


Fig. 1. Schematic  $p$ - $t$  diagram for  $\alpha$ -Phytosteryl-Isobutyrate.

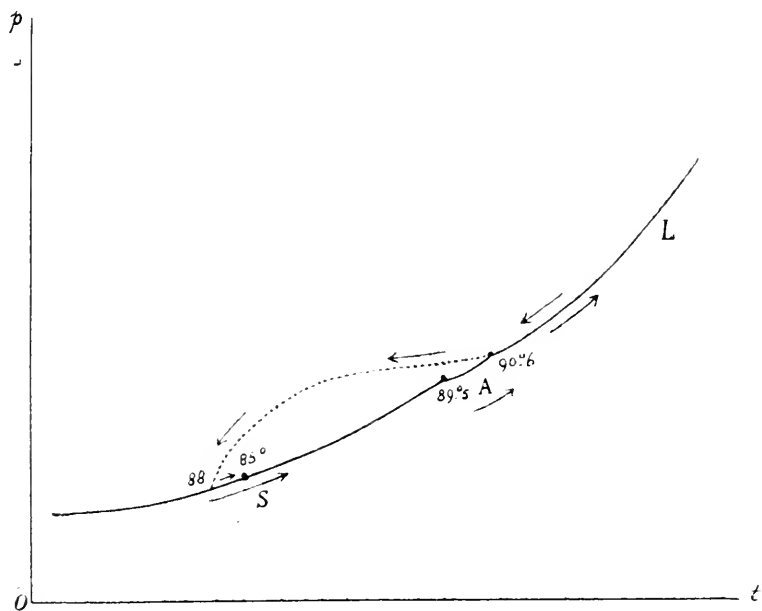


Fig. 2. Schematic  $p$ - $t$  diagram for  $\alpha$ -Phytosteryl- $n$ -Butyrate.

thermometric method is certainly preferable to the microscopic one, because in the latter, the delicate changes in temperature cannot be controlled so surely as in the first method. For this reason, the phase-

transformations, when observed microscopically, convey the impression of being more *sudden* than in the thermic observation.

Still, the microscope completes the task of the thermometer in a manner not to be undervalued, at it gives an insight into the structure of the diverse phases and allows one to demonstrate their difference or their identity.

§ 5. If a little of the beautifully crystallised *n-valerate* is carefully melted on an object glass, the substance, at a definite temperature changes, apparently suddenly, into an aggregate of an enormous number of globular, very large and strongly doubly-refracting liquid-drops, which all exhibit the black cross of the spherulites <sup>1)</sup> but can flow really all the same. This condition may be rendered permanent for a long time at will. But they may also amalgamate afterwards to larger, plate-like, highly coloured liquid individuals, somewhat resembling sharply limited crystals. These are frequently multiplets of liquid drops: the demarcations between the separate individuals vary constantly by changes in temperature.

The isotropous border of the mass is very striking. By pressure or by moving the covering glass, also by the sliding currents which we can induce herein by changes in temperature, it may be readily shown that this isotropous border, owing to a parallel orientation of the liquid individuals, is only pseudo-isotropous and really identical with the rest of the phase. Sometimes one may succeed even in communicating this pseudo-isotropous aspect to the entire mass <sup>2)</sup> by

<sup>1)</sup> We can, however, often observe a slanting projection of the optical symmetry axis, which gives the same impression as if we look perpendicularly to one of the optical axes of a biaxial crystal, or on a monoxial crystal cut obliquely to the optical axis. We observe at the same time coloured rings which exhibit an elliptic form. It is very remarkable that, when the phase has become very viscous on cooling, these ellipsoidal drops, provided with rings and slanting but mutually parallel-directed axes may be kept for a long time in an apparently immobile condition in the midst of the pseudo-isotropous or double-refracting liquid. They place themselves mutually like little ellipsoidal magnets.

However, I could observe, that these drops are often not quite ellipsoidal, but that they are sharply broken a little at the one side, just there, where the optical axis is slanting. By turning the object-table, the axial point turns in the same direction as the table, while the black line or cross is preserved. (Added in the English translation Januari 1907).

<sup>2)</sup> The anisotropous-liquid phase has, in the case of the two valerates, an extraordinary tendency to place itself in this pseudo-isotropous condition. We can observe this, because the border of the drop often moves inward with widening of the isotropous-looking line. It is also remarkable to see how the flowing crystals when meeting an air bubble arrange themselves close together, normally on the border thereof.

often repeated warming followed by rapid cooling. This substance is about the best known example of this phenomenon.

§ 6. If now we go on heating very cautiously, the larger flowing crystals and also the smaller drops situated between them are seen to move about rapidly: the larger individuals, which consist mostly of twins or quadruplets, are split up into a multitude of globular drops and these, together with the smaller ones, disappear at a definite temperature entirely in the isotropous liquid, which is now isotropous in *reality*. The globules of the liquid rotate to the right and the left under distortion of the mass, as may be observed from the spiral-shaped transformation of the black cross. Sometimes, before the mass becomes isotropous we may notice a temporary aggrandisement of the plate-like flowing crystals at the expense of the smaller interjacent globules; a result of the momentarily increased crystallisation-velocity due to heating.

§ 7. On cooling the isotropous fusion this is first differentiated into an infinite number of the double-refracting liquid globulus, which here and there amalgamate to the more plate-like flowing crystals. On further cooling, these latter individuals remain in existence notwithstanding the undercooling, while the little globules in the meanwhile unite to the same kind of plate-like individuals. This aggregate, brilliant in higher interference colours becomes in course of time thicker and thicker in consistency while the aggregation, owing to an apparent splitting, becomes more and more finely granulated. But even after the lapse of some hours, the phase remains anisotropous-liquid as may be easily proved by shifting the mass and by the pseudo-isotropous border, which commences to exhibit delicate, double refracting current-lines. In the end when the pseudo-isotropous liquid has passed like the remainder into the same, almost completely immobile aggregation of doubly-refracting individuals, it is, gradually, transformed after a very long time into an aggregate of plates and spherulite-like masses, which possess a strong double refraction.

§ 8. If, after the lapse of some hours, the partially or completely solidified mass is melted cautiously, we sometimes succeed, in the case of the two *calceates*, in keeping the crystals of the phase *S* (therefore the *solid* crystals) for a few minutes near the isotropous fusion *L* at a temperature above the highest transition point. This phenomenon is, therefore, again quite homologous to that first observed by me with *cholesterol-laurate* and which might be described as a

*heating of a solid substance S above its melting point without fusion taking place.* For the present, at least according to existing ideas, this behaviour can only be explained by assuming the presence of a two-component-system with tautomeric transformations subject to a strong retardation.

When the isotropous fusion *L* which has scarcely cooled to a few doubly-refracting drops is melted cautiously, we may observe sometimes that where a moment before the strongly luminous, yellowish-white globules were visible, there are now present greyish globules showing the black cross, which gradually decrease in size and also darken, to disappear finally as (isotropous?) little globules in the isotropous fusion <sup>1)</sup>. This phenomenon, in connection with those of crystallised ferric chloride to be described later, and with similar phenomena observed with the cholesterol esters appears to me to have great significance for the theory of the formation of liquid crystals.

§ 9. Finally, there is something to be observed as to the separation of *α-Phytosterol-valerate* from organic solvents. The substance may be obtained from ethyl acetate + a little alcohol in beautiful, hard, well-formed little crystals. If, however, the saturated *cold* solution in ethyl acetate is mixed with much acetone (in which the substance is but sparingly soluble) the liquid suddenly becomes a milky-white emulsion which deposits the compound *not* as a fine powder, but in the form of a *doubly-refracting, very thick and very sticky liquid*.

I have repeated this precipitation in a hollow object glass under the microscope. The emulsion consists of a very great number of doubly-refracting, globular liquid-globules, which are either moving about rapidly in the liquid, or, when united to larger masses, are quite identical with the ordinary anisotropous phase *A*, when this is cooled to the temperature of the room. These little globules all exhibit the cross of the spherulites, and the doubly-refracting liquids. They soon become solid and then form small needles and spherulitic aggregations. It may be easily proved by stirring that the globules deposited first are liquid; moreover, the doubly-refracting masses often communicate with each other by means of very narrow, doubly-refracting currents, while they often exhibit the phenomena of pseudo-isotropism.

Therefore, we have evidently obtained here the liquid-anisotropous

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<sup>1)</sup> Before that happens, we may sometimes see here the globules becoming enlarged to multiplets by amalgamation there larger ones being changed into smaller ones, sometimes here one disappearing in the liquid while very close by new individuals appear.

phase *A* from a solution by rapid precipitation at the temperature of the room, and that in isolated drops! A few other phytosterol esters exhibit analogous phenomena which I will describe later on in a more elaborate communication on these substances.

§ 10. A very remarkable fact in the *n-valerate*, the *iso-valerate* and the *isobutyrate*, is the differentiation of the isotropous fusion into a large number of globular, doubly-refracting liquid drops of considerable dimensions, which like the circles of fat on soup float alongside and over each other and often unite to multiplets, whose separate parts are still recognisable. Wreathed aggregations of the liquid globules are also observed occasionally. In most cases the separate liquid globules exhibit the black cross and the four luminous quadrants grouped centrally. They are, however, also seen to roll about frequently, so that the projection of the optical symmetry axis now takes place eccentrically. Owing to the enormous size of the individuals and the low temperature-limits, these esters lend themselves to the study of these phenomena certainly VORLÄNDER'S *p*-azoxybenzoic-ethylester.

If the temperature of the mass, when totally differentiated into liquid globules — and the *isobutyrate* is particularly adapted for this differentiation — is slightly raised, the liquid globules are often seen to disappear suddenly just after they have enlarged their limits as it were by an expansion. It is like a soap-bubble bursting by over blowing.

§ 11. Finally, I wish to observe that the thermal transitions just described and particularly those of the two *valerates*, can only be interpreted by assuming a quite continuous progressive change. For all these gradual transformations, either on melting or on solidifying, a measurable time is required and nowhere is to be found any indication of a sudden leap. An exception is, however, afforded by the sudden crystallisation of the two *butyrates*.

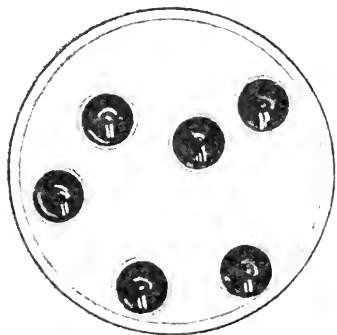
§ 12. As regards the differentiation of the fusion *L* into an aggregate of anisotropous liquid globules, I will now make a communication as to an experiment upon the crystallising of *ferric chloride hexahydrate*, which substance exhibits something similar, and which, like most undercooled fusions and like many compounds which exhibit liquid crystals, crystallises in typical spherulites.

If we melt the compound  $\text{Fe}_2\text{Cl}_6 + 12\text{H}_2\text{O}$  cautiously in a little tube, taking care that no water escapes, and a drop of this brownish-



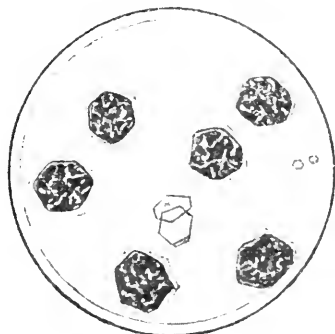
red fusion is put on an object glass, it may be left for hours at the temperature of the room without a trace of crystallisation being noticed. The liquid is now greatly undercooled and exists in a state of metastable equilibrium. For all that, it has the same chemical composition as the solid phase from which it was formed.

On prolonged exposure, *small liquid globules* appear locally in the fairly viscous mass, probably owing to local cooling, or by a spontaneous evaporation of water at those points. These liquid globules are quite isotropic and are surrounded by a delicate aureole having an index of refraction different from that of the rest of the liquid (fig. 3*a*). The observation shows that, optically, they are, practically, no denser than the liquid, and from the fact that they afterwards become, *in their entirety*, a spherulite of the hexahydrate, we must

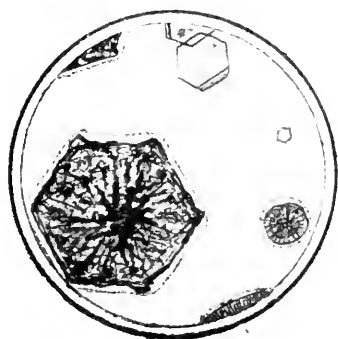
Fig. 3*a*.

conclude that their chemical composition does not differ from that of the fused mass.

These globules of liquid are converted gradually into doubly-refracting masses whose section is that of a regular hexangle with rounded off angles: individual crystals are not yet visible in the doubly-refracting mass and the luminous zone around still appears to exist (fig. 3*b*).

Fig. 3*b*.

Here and there, hexangular, sharply limited, very small plate-shaped crystals are also seen to form in the liquid without previous formation of liquid globules<sup>1)</sup>. In the end, the doubly-refracting hexangular mass gets gradually limited by more irregular sides, while a greater differentiation of the mass into light and dark portions points to a crystallisation process commencing and progressing slowly.

Fig. 3*c*.

<sup>1)</sup> These may, however, be formed perhaps owing to the presence of traces of sal ammoniac.

Finally, we can observe a *spherolite* of the hexahydrate with a radial structure which now grows centrifugally to the large well-known semi-spheroidal spherolites of ferric chloride (fig. 3c).

§ 13. This experiment proves that the abrogation of the metastable condition, or at all events of a liquid condition which is possible under the influence of *phenomena* of retardation may happen owing to the formation of *spherolites which are preceded by the differentiation of the fusion into an aggregate of liquid globules*. True, the latter are here isotropous in contrast with the phytosterol esters just described, but the anisotropism of the latter liquids may be caused also by factors which are of secondary importance for the apparently existing connection between: metastability of liquid conditions, their abrogation by spherolite formation and the possible appearance of liquid globules as an intermediate phenomenon. I will just call attention to the fact that if we set aside a solution to crystallise with addition of a substance which retards the crystallisation, this will commence with the separation of originally isotropous liquid globules, so-called globulites, which BEHREND and VOGELSANG commenced to study long time ago.

All this leads to the presumption that the formation of the anisotropous liquid phases as aggregates of doubly-refracting liquid globules may have its origin in a kind of *phenomena* of retardation, the nature of which is still unknown to us at the present. Before long, I hope to revert again to this question.

Zaandam, 21 Nov. 1906.

**Physics.** — “Some additional remarks on the quantity  $H$  and MAXWELL’s distribution of velocities.” By Dr. O. POSTMA. (Communicated by Prof. H. A. LORENTZ).

§ 1. In these proceedings of Jan. 27<sup>th</sup> 1906 occur some remarks by me under the title of: “Some remarks on the quantity  $H$  in BOLTZMANN’s Vorlesungen über Gastheorie”.

My intention is now to add something to these remarks, more particularly in connection with GIBBS’ book on Statistical Mechanics <sup>1)</sup>, and a paper by Dr. C. H. WIND: “Zur Gastheorie” <sup>2)</sup>.

In my above-mentioned paper I specially criticised the proofs given

<sup>1)</sup> J. WILLARD GIBBS “Elementary Principles in Statistical Mechanics”, New-York, 1902.

<sup>2)</sup> Wien. Sitzungsber. Bd. 106, p. 21, Jan. 1897.