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Physics. — “Contributions to the study of liquid crystals. III. Melting and congelation-phenomena with para-azoxy-anisol.” By Dr. W. J. H. MOLL and Prof. L. S. ORNSTEIN. (Communicated by Prof. W. H. JULIUS).

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In our second paper on the extinction of liquid crystals we observed, that among others with para-azoxy-anisol there is, with regard to the extinction, a difference between the liquid crystalline condition which arises by melting the solid crystals (“exsolid”) and that which arises in cooling the isotropic liquid (“exliquid”). Where with para-azoxy-anisol we had stated the existence of two solid phases, the question lay at hand whether in exsolid and exliquid we had perhaps got two different liquid crystalline phases. To make this out a research after the exact position of the points of transition was desirable.

Method of Research.

There we made use of a kind of radiation calorimeter, which is schematically represented in figure 1. The substance to be examined (about $\frac{1}{4}$ c.m.³) half filled a gold beaker *M* with thin walls, against which on the exterior on the one side a brass wire, on the other a constantane wire has been soldered. The two wires form a thermoelement, by the help of which the temperature of the beaker and its contents is measured ¹⁾ and serve at the same time to hang it within a brass cylinder. This

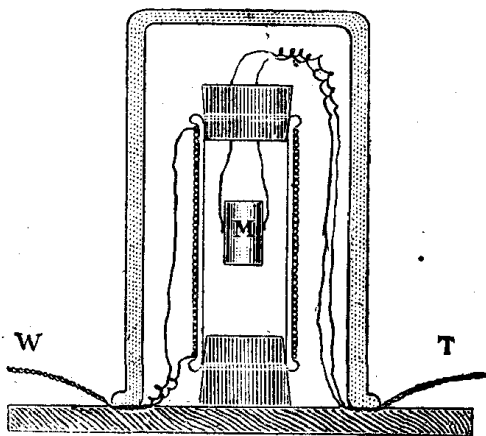


Fig. 1.

¹⁾ Before we came to this way of fixing up the “thermobeaker”, we had followed the usual method for our determination of the temperature, i.e. we had placed a thermometer and later on a thermoelement within the substance to be melted. Then a number of “Schmutzeffecte” were produced, which on close investigation had to be ascribed to convection currents. Our method is of course quite free from this disturbance.

cylinder is closed by a cork at the top and one at the bottom and, that it may be heated electrically, it is provided with a layer of isolated wire. The whole stands on a little table under a glass, which only allows of passage to the wires of the heating-current W and those of the thermocurrent T .

The research consisted in the determination of the temperature-time curve with a constant heating current. If this heating current is closed, the temperature first rises quickly, then more slowly and asymptotically approaches a limit value. If now (also before the limit-temperature is reached) the heating current is weakened and then kept constant, the temperature first falls rapidly, then more slowly till a second lower limiting temperature is reached.

When within the temperature-region in observation the substance in the beaker melts, congelates, or in general undergoes some change of phase, this will be observable on the T - t curve. So during the supply of heat to the beaker the melting will appear as a sharp twist in the ascending branch. The place of the twist indicates the melting-temperature and, that with a much higher degree of accuracy, than would even be possible with a measuring of the temperature within the substance.

The second contact place of the thermo-element was in melting ice during the time of observation. The thermo-current was measured by a quick-indicating galvanometer of MOLL. To keep the deviations within bounds the thermoforce was first for the greater part compensated with the help of a constant current-source and a shunt, and besides the sensitiveness of the galvanometer was strongly reduced.

The deviations of the galvanometer were registered and the T - t curves thus photographed. The figures 2—6 are reduced reproductions of our original photos. The figures put underneath give in an arbitrary measure the temporal value of the heating-current.

An abscisslength of 8 cm. corresponds to a quarter of an hour.

The dotted line indicates the same temperature of about 118° in the different figures.

Discussion of the Results.

Fig. 2. The two ascending branches fully agree and at A the first point of transition shows itself sharply, i.e. the melting point of the solid substance. This temperature, which amounts to about 118° , we have always chosen as point of departure. The strong oscillations

of temperature at *B* are without importance for our investigation and may be left apart¹⁾.

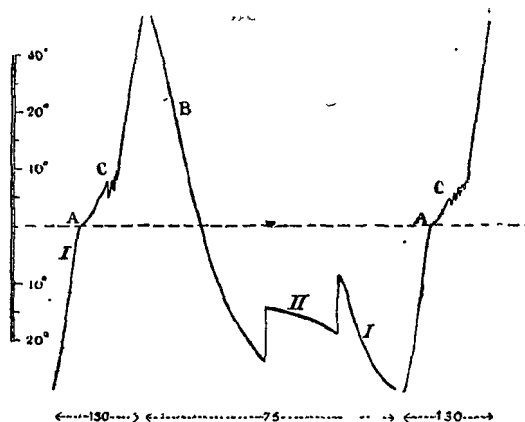


Fig. 2.

The second point of transition is difficult to observe in the ascending branch on account of its steepness, in the descending branch it appears more clearly at *B*. Further we observe in the descending branch a strong undercooling to far below 100° and then a sudden development of heat and congelation. The highest temperature reached in this process ($13^{\circ},5$ below the zero-line) is the point where a very unstable solid phase congeals, which we shall call phase II (phase I has the melting point at about 118°), and which after a short time spontaneously and under the development of heat passes into another

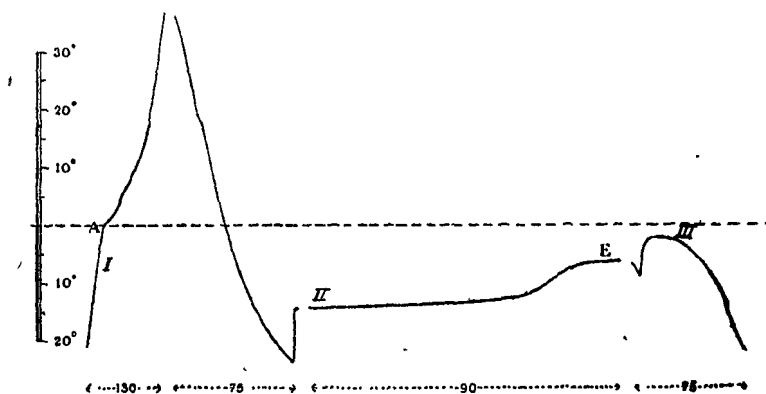


Fig. 3.

¹⁾ They have their cause in the fact that the volume of para azoxy-anisol changes considerably in melting. The internal sidewall of the beaker gets for this reason detached from its contents and can temporarily rise to a higher temperature, so that a drop, dripping from the solid centre, again occasions a sudden falling of the temperature.

phase. Probably directly into phase I, for at a supply of heat the same melting point of about 118° shows itself.

Fig. 3. After the same initial development as in the case represented by fig. 2 the same deep undercooling is again followed by the appearance of the solid phase II. But now we have to take care that immediately after this phase arises, heat is supplied by strengthening the heating-current, and that to such value that phase II is melted but the arising liquid crystalline phase remains undercooled. Whilst at E its temperature has become constant, we have, in order to hasten the process of congelation, reduced the heating-current, and in result of this the temperature has scarcely fallen a few degrees before under the development of heat the liquid crystalline substance congeals and now at a temperature of 2° below the zero-line. We call this new condition solid phase III.

Fig. 4 also gives the origin of phase III from the undercooled

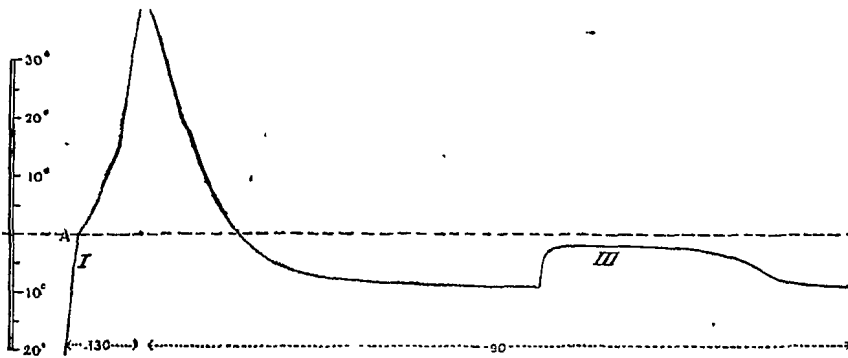


Fig. 4.

liquid crystalline phase. The heating-current during the preceding cooling was chosen in such a way that the formation of phase II was excluded.

Fig. 5 gives once again the origin of plate III with the exclusion of phase II. But where the undercooled liquid crystalline phase in fig. 4

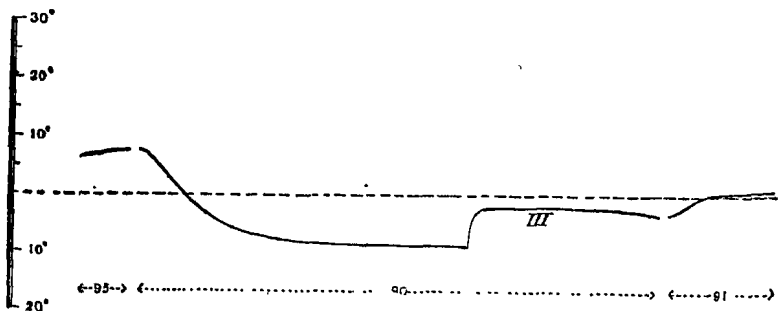


Fig. 5.

was ex-liquid, we have taken it ex-solid in fig. 5. Besides this figure also gives the melting of phase III and there the remarkable pheno-

menon presents itself, that phase III melts at a temperature which we know as the melting point of phase I. Thus it is shown that in this way phase III, during its formation, gradually passed into phase I.

Fig. 6 is reproduced as it allows of studying the second point of transition. At *F* ex-solid, at *G* ex-liquid pass into the isotropic

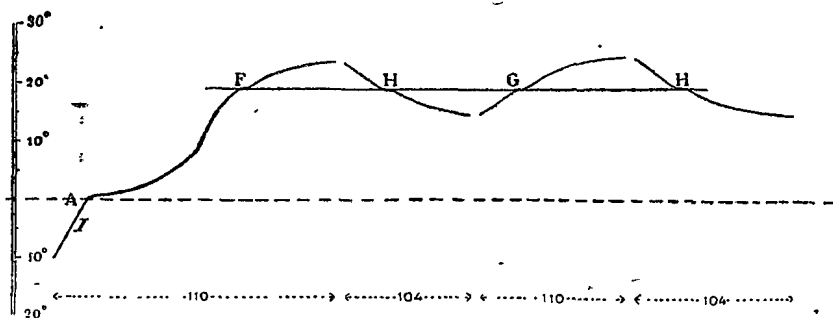


Fig. 6.

phase under the absorption of heat, *H* gives the phenomenon of transition while heat is developed and the three transitions *F* *G* and *H* happen really at the same temperature.

CONCLUSION.

Whilst thus, as far as the situation of the points of transition is concerned, we have found no indication of a difference between exsolid and exliquid with para-azoxy-anisol, we have discovered several phases in the solid condition of aggregation in our investigation. Beside the three phases which we have distinguished as I, II and III, there certainly still exists a fourth¹⁾, with a melting-point of about 108°. It seems that this phase, which during this investigation never once showed itself, can only exist in capillary layers (between glass).

This short, more or less schematic summing up of the most striking facts, which present themselves in an investigation of the melting- and congelation phenomena of para-azoxy-anisol, must suffice, however interesting a closer examination of this substance and perhaps of other substances according to the method indicated may be from a standpoint of phase-theory, for our interest is greater for problems of a different nature.

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Utrecht, September 1917.

¹⁾ Cf. our second contribution. Verslag Kon. Acad. v. Wetensch. XXV, p. 1114.