

Physics. — “*On crystallized Nitrogen*”. By D. VORLÄNDER and W. H. KEESOM. (Communication N^o. 182c from the Physical Laboratory at Leiden).

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§ 1. *Introduction.* According to WAHL ¹⁾ nitrogen when solidifying out of the liquid state at -210° crystallizes in the cubic system and is optically completely isotropic. On the other hand DE SMEDT and KEESOM ²⁾ have examined the structure of crystallized nitrogen by Röntgen analysis at -253° and found that in all probability at this lower temperature the nitrogen is not cubic. EUCKEN ³⁾, as well as KEESOM and KAMERLINGH ONNES ⁴⁾ had already established the fact that at $35^{\circ}.5$ K. a transformation takes place.

According to these results nitrogen would belong to that important class of dimorphic substances, in which the cubic form which arises at higher temperature passes at falling temperature enantiotropically into an optically anisotropic form. Nitrogen would therefore behave in the same way as white phosphorus ⁵⁾.

§ 2. *Micro-observations at temperatures down to -253° C.* We investigated whether by means of a microscope in parallel polarised light a characteristic transformation isotropic \rightleftharpoons anisotropic could be ascertained in nitrogen and in some other substances crystallizing in the cubic system when cooled to -253° . After overcoming the initial difficulties we were able to observe the substances, cooled in a stream of cold hydrogen or plunged in liquid hydrogen, between crossed nicols. In the mean time experiments with cubic substances ⁶⁾ of very various nature, and further observations on a few anisotropic substances had shown that at these low temperatures a large harvest of new forms was not to be anticipated; the transformation isotropic \rightarrow anisotropic in particular, did not take place. Ammoniumchloride for which SIMON ⁷⁾ thought to have found a trans-

¹⁾ W. WAHL, Proc. Roy. Soc. A **87**, 371, 1912; A **88**, 61, 1913; Z.S. physik. Chem. **84**, 106, 1913.

²⁾ Physica **5**, 344, 1925; Leiden Comm. N^o. 178b.

³⁾ A. EUCKEN, Verh. d. D. physik. Ges. **18**, 4, 1916.

⁴⁾ These Proc. **18**, 1247, 1916; Leiden Comm. N^o. 149a, p. 8, note 2.

⁵⁾ D. VORLÄNDER, Ber. d. D. chem. Ges. **58**, 1802, 1925.

⁶⁾ Gold, iron, silver, diamond, KCl, KBr, KJ, NaCl, NH₄Cl, TiCl, TlBr, CaF₂, K₂PtCl₆, As₂O₃, (NH₄)₂SnCl₆, (NH₄)₂TeCl₆, ferric-ammonium-, thallium- and potassium-alum, spinel, corundum, ruby, zinblend, analcym, pyrope.

⁷⁾ F. SIMON, Ann. d. Phys. (4) **65**, 264, 1922; c.f. W. EITEL, Fortschr. d. Mineralogie **8**, **34**, 1923, according to whom the transformation of ammonium chloride “extends over a large temperature range and cannot be demonstrated dilatometrically”.

formation point at -243° while measuring the molecular heat, remains down to -253° optically isotropic; common and blue rock salt remain unchanged; pleochroic solid crystals retain their pleochroism¹⁾; ice remains hexagonal between 0° and -253° .

What we observed in the anisotropic substances²⁾ through the microscope was principally some changes which gradually took place in the volume and the double refraction with rising and falling temperatures and the formation of cracks in the material, but no ordinary dimorphic transformations, which should take place with a complete change in the crystalline structure with a distinct, even if slow, growth, from the one to the other form. In this way we observed under the microscope for the space of $1/2$ to $3/4$ hour several preparations plunged in liquid hydrogen. This does not entirely exclude the possibility of transformations still taking place, but we regard it as highly improbable, when we consider further that during a very slow re-heating of the substances no transformations were observable.

§ 3. *The preparation of pure nitrogen.* For these experiments with nitrogen the vital thing was to procure the gas absolutely pure. This was done from ammonium nitrite, by a gradual introduction of a concentrated aqueous solution of sodium nitrite (1 equivalent weight) through a dropping funnel into an aqueous solution of ammonium sulphate (2.5 equivalent weight) and yellow potassium chromate³⁾ (1 equivalent weight) heated on a water bath to 80° — 95° ⁴⁾. To expel the air from the apparatus (the solutions having been previously boiled) two of these nitrogen generators were connected in series; they were set working one after the other, after having been washed through with commercial nitrogen and the whole of the rest of the apparatus evacuated. This consisted of glass tubes sealed together, with the exception of the taps to the oxidation tube, which were closed by mercury. The nitrite nitrogen from the generators ran through the following apparatus:

1. two vessels cooled in icewater, containing 5 volumes saturated solution of potassium bichromate and 1 volume concentrated sulfuric acid, to oxidise oxides of nitrogen;
2. two tubes filled with pieces of sodium- or potassium hydroxide;
3. two drying vessels cooled with liquid air, to freeze out water vapour, NO, etc.

¹⁾ Undercooled pleochroitic mono-axial layers of liquid crystals (cyano benzalamino-cinnamic active amyl ester) changed into a fine net-work with very irregular boundaries, while loosing their pleochroism.

²⁾ Sulphur, phosphorus, bromine, iodine, $\text{Pb}(\text{NO}_3)_2$, CdJ_2 , SbJ_3 , TlJ , Hg_2Cl_2 , K_2PtCl_4 , AsBr_3 , H_3BO_3 , ZnO , gypsum, arragonite, Iceland spar, quartz, beryl, tourmaline, dichroite, JCN , $(\text{CH}_3)_4\text{N}$, $\text{Hg}(\text{CN})_2$, CCl_4 , CHBr_3 , normal heneicosane, hexadecylene, norm. valeric acid, stearic acid, elaidic acid, tristearine, norm. hexylalcohol, cyclohexanone, methyloxalate.

³⁾ C.f. VON KNORRE, Chem. Industrie 25, 531 and 550, 1902.

⁴⁾ C.f. H. KAMERLINGH ONNES and A. TH. VAN URK. Leiden Comm. No. 169d and A. TH. VAN URK, Diss. Leiden, 1924, p. 21.

4. an oxidation tube heated in a gas oven to low red heat, provided for $\frac{4}{5}$ of its length with copper gauze and for $\frac{1}{5}$ with CuO;
5. two drying vessels cooled outside with liquid air (one of them was a spiral glass tube);
6. two condensation vessels cooled outside by liquid air, boiling under reduced pressure; the nitrogen was liquefied in the first of these vessels and then distilled over into the second vessel (after the surrounding liquid air had been brought back to atmospheric pressure).

The nitrogen was then distilled over, into a previously evacuated

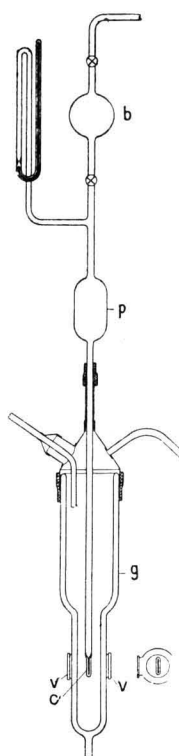


Fig. 1. The nitrogen condensed in the first condensation vessel (No. 6) formed a clear, colourless liquid which showed no trace of turbidity and when distilled off left no trace of foreign matter. After washing, the nitrogen was fractionally distilled over from the first condensation vessel into the second (No. 6); then the pipette with observation chamber was filled with it, up to about 40 cm pressure. This nitrogen contained no oxygen or oxide of nitrogen (tested with alkaline solution of pyrogallol and when admitting air, with acidified potassium iodide). By sealing on in front of the pipette a glass bulb (*b*) filled with nitrogen under increased pressure (80 cm) the possibility of oxygen from the outer atmosphere penetrating through the tap of the pipette was prevented. In the observations with the polarisation microscope the chamber was placed in a cryostat glass, of which the inner wall was cylindrical, while on the outer wall at the height of the chamber two plane parallel glass windows were made. The nitrogen crystallized on being cooled with hydrogen, to a layer of 0.2 to 0.3 mm thickness in the observation chamber²).

§ 4. *Observations of the crystallized nitrogen in the polarisation microscope.* As the nitrogen crystallizes out from the liquid by cooling, the first particles of solid nitrogen still moving in the liquid appear to be double refracting. Shortly after the whole mass has become doubly refracting and solid, a marked contraction, of roughly from $\frac{3}{4}$ to $\frac{4}{5}$ of the original

¹) Simple mercury manometers, acting at the same time as safety valves, were placed: a. between the generator and N^o. 1; b. between N^o. 5 and N^o. 6; c. between the first and the second vessel of N^o. 6; d. behind N^o. 6; e. at the pipette.

²) We wish to express our thanks to Mr. W. PLOEG for his help in preparing the pure nitrogen.

volume of the fluid takes place. The solid optically anisotropic mass is strongly deformed, while forming tubular and vermiform holes, from the surface of which often innumerable very minute and branched cracks and holes spread out, which between crossed nicols appear black. Pleochroism could not be observed at the transparent surfaces when rotating the polarisor, the other nicol being removed. The mass which seems to be principally fibrous and in some places tabular, shows no perceivable definite structure, so that the existence of definite angles or extinction directions could not be observed. On further cooling the double refraction changed. At the introduction of a gypsum plate 1st order, red polarisation colours changed into yellow, violet into blue. This change takes place gradually; at the same time a few fairly rapid changes were seen, in which a fine seam appeared to run over the mass. A distinct transformation from one optically anisotropic form into another could not be ascertained. A transformation from an isotropic to an anisotropic phase from the first crystallization at -210° to -253° , is excluded.

With rising temperature first the changes of the polarisation colours in the opposite sense are seen; after that, on approaching the melting point, the holes partly fill up, so that a clear tabular crystalline mass forms, in which no special direction of growth can be ascertained, as is the case with falling temperature, as apparently the crystalline particles are orientated and grown together in every possible direction. The pattern that is formed is very peculiar, we do not remember ever to have seen one like it in ordinary crystalline masses of other substances. Now the melting begins very speedily, during which the solid "tables" remain optically anisotropic to the last particle, floating in liquid nitrogen. It thus appears that here too there is no isotropic phase. These observations make it quite clear that the double refraction which was observed could not be only due to deformation, caused by the contraction of an isotropic form.

§ 5. By the observations described in § 4 the cooling in the stream of cold hydrogen and in liquid hydrogen respectively took place fairly quickly. As Dr. TERPSTRA pointed out to us it was possible that with rapid cooling anomalous forms would arise. We have therefore repeated the observations to about -218° in a bath of oxygen, boiling under reduced pressure. By regulating the pressure of this we could regulate the rapidity of the crystallization as well as that of the re-heating.

In these experiments, in which Dr. TERPSTRA was so kind as to take part, the nitrogen was observed: 1. with an ordinary microscope, 2. with crossed nicols in // light, 3. with crossed nicols and a gypsum plate red 1st order in // light, 4. in a conoscope with convergent light.

The following observations were made:

1. With the microscope the coagulation in the field of vision could

be seen gradually proceeding, mostly in a few // fields with progressing boundaries about \perp to the meniscus of the liquid. The fields were often directly distinguishable on account of the difference in intensity of the light let through.

2. Between crossed nicols the differences in intensity of the fields could not be fixed with certainty. Neither could differences during synchronic rotation of the nicols be observed. The thickness of the crystal layer was about 0.3 mm, the visible field formed a circle of 5 mm diameter.

3. With the gypsum plate changes of colour usually occurred, which indicated a very weak double refraction. Occasionally a field was observed without perceptible double refraction, between others which were distinctly doubly refracting.

4. Conoscopic investigation yielded only negative results. Neither cross, rings or hyperboles were observable. Rotation of the analysor showed that optical activity played no part.

A repetition of observations 1—3 by Messrs ESBACH and PLOEG with nitrogen prepared from sodium azide led to the same conclusions.

§ 6. *Conclusion.* The observations given in §§ 4 and 5 lead to the conclusion that nitrogen immediately at the melting point is doubly refracting. The double refraction is extremely small.

The fact that WAHL did not find any double refraction may be due to his having used a layer only $\frac{1}{20}$ mm in thickness, and making his observations only with crossed nicols, and not with the more sensitive method of the gypsum plate.

Crystallized nitrogen cannot therefore be compared to the dimorphic white phosphorus. Its anisotropic structure corresponds better with the multivarious chemical properties of nitrogen than would be the case with the regular structure so far assumed.

§ 7. *Observations on crystallized argon.* In agreement with WAHL's results ¹⁾ and with the Röntgen analysis of F. SIMON and CLARA VON SIMSON ²⁾ and of DE SMEDT and KEESOM ³⁾ argon according to our experiments is regular to -253° . The manner of crystallizing is very different from that of nitrogen. Argon freezes to an optically isotropic homogeneous mass, which with more intense cooling shrinks as a whole and often springs off from the walls of the observation chamber without becoming doubly refracting.

On being gradually heated the crystallized argon of our experiments began to sublime strongly. The glass wall visible above the crystalline

¹⁾ See p. 1069, note 1.

²⁾ F. SIMON and CLARA VON SIMSON, *Z.s. f. Physik* **25**, 160, 1924.

³⁾ See p. 1069, note 2.

mass was covered with small isotropic crystals, as well as with needles which were grown together at right angles to each other. After that the argon melted.

To conclude we are glad to express our thanks to Mr. V. ESBACH for the great help that he has given us, and to H. VORLÄNDER for his help in part of these experiments.
