Citation:

Johannes Diderik van der Waals, On the point in which the solid state disappears as an answer to the question in how far this point can be compared to the critical point of a liquid. The easiest way to do this is by means of the ?-curve, in:
KNAW, Proceedings, 16 I, 1913, Amsterdam, 1913, pp. 39-40

this pseudo-system, as well with regard to the gaseous as to the liquid and the solid phase.

The phenomenon, observed here with great probability, of internal equilibrium between structure isomers will be of pretty general occurrence without any doubt, so that it will not be difficult to discover many more interesting examples, which are accessible to experiment.

Anorg. Chem. Lab. of the University.

Amsterdam, May 27, 1913.

Physics. — *"On the point in which the solid state disappears as an answer to the question in how far this point can be compared to the critical point of a liquid. The easiest way to do this is by means of the ψ-curve".* By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of February 22, 1913).

If the ψ-curve is drawn at the triple point, the same straight line is touched by: 1. the ψ-curve liquid-vapour, 2. the ψ-curve for the solid substance. Let us put the case that occurs most frequently, in which $v_s < v_l < v_g$. On rise of the temperature the ψ-curves descend, but not in an equal degree. The liquid-vapour curve descends more than the curve for the solid substance. Relatively ψ_s ascends therefore. And accordingly the tangent for the coexisting states liquid-vapour, and that for the coexisting states liquid-solid are separated. The pressure has increased, but that for the coexistence solid-liquid far more than for the coexistence liquid-vapour. When the temperature continues to rise the ψ-curve for the liquid will more and more approach the ψ-curve for the solid substance, and it will reach it at the temperature at which the solid state disappears at infinite pressure. At the critical point liquid-vapour these two states are identical; the solid state on the other hand has been expelled by the liquid state. This, however, takes place at a pressure equal to infinity and so a volume equal to v_0. Above this temperature the solid state no longer exists, but the liquid state does. I have shown elsewhere, however, that then, when the pressure again approaches infinity, and hence the volume to v_0, the viscous-solid state will probably appear.

If we now consider the case, in which, as for water and ice $v_s > v_l$, the p,T-line for the coexisting phases runs from the triple point to lower temperatures. Now two cases are possible, viz. that this line continues to proceed to lower temperatures, and p continues to rise to infinitely great; or that after having reached certain minimum of temperature, it proceeds to higher temperatures, again before p has become infinitely great. If the latter should be the case there is in the p,T-line of the coexistence a point in which $\frac{dp}{dT}=\frac{\eta_l - \eta_s}{v_l - v_s}=\infty$, or $v_l=v_s$. And for the points of the line of coexistence which lie higher, v_l has then become $> v_s$, and the above described case occurs again. Nor is there a difference of significance when v always remains greater than v_l. At the temperature of the disappearance of the solid state, which is then lower than the temperature of the triple point, this disappearance takes place at a pressure equal to infinity. Since, however, v_s is always greater than v_l, we can hardly continue to speak of "expelled". The volumes v_s and v_l have now however both become equal to v_o, and on rise of the temperature it is again only the liquid which can exist.

Assuming here again that liquids under a very high pressure, and so in a very small volume, almost equal to v_o, assume the viscous state, we might point out the following difference. If $v_s < v_l$ these substances have the solid state in volumes which are little greater than v_o at temperatures somewhat below that of the disappearance of the solid state; they have the viscous state on increase of volume, and on further increase of the volume they have the liquid state. If on the other hand $v_s > v_l$, the succession of the 2 solid states is reversed.

At the highest temperature for the existence of the solid state the difference between solid and viscous has probably disappeared under infinite pressure.

Physics. — *"On a system of curves occurring in* EINSTEIN'S *theory of gravitation"*. By Ch. H. VAN Os. (Communicated by Prof. H. A. LORENTZ).

In Prof. P. EHRENFEST's communication on EINSTEIN's gravitation theory (Vol. XV, p. 1187) a system of ∞^2 curves occurs which is determined by the condition that a hyperboloid:

$$H \equiv A(x^2 + y^2 - z^2) + Bx + Cy + Dz + E = 0, \quad . \quad . \quad (1)$$

a so-called "light hyperboloid" can always be brought through two of these curves. This system will be examined more closely here.

The curves are intersections of the hyperboloids H. As they must also have a conic $K\infty$