

Citation:

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Physics. — “*On the solid state.*” IV. By Mr. J. J. VAN LAAR. Communicated by Prof. H. A. LORENTZ.

13. In the paper in the Arch. Teyler already cited a few times, I derived in § 6 (p. 34—35) the formula for the pressure of coexistence of two arbitrary phases (liquid-vapour, liquid-solid), when *association* is assumed in both phases.

I will just state the derivation of this fundamental formula here once more.

For equilibrium between two coexisting phases the molecular thermodynamic potentials of the components must be the same in the two phases. If these components are distinguished by the indices 1 (complex molecules) and 2 (simple molecules), we have e.g. in our case

$$(\mu_1)_{liq} = (\mu_1)_{solid} \dots \dots \dots (a)$$

On account of the relation of equilibrium $\mu_1 = 2\mu_2$ in both phases naturally $(\mu_2)_{liq} = (\mu_2)_{solid}$. Now

$$\mu_1 = C_1 - \frac{\partial \Omega'}{\partial n_1} + RT \log c_1, \dots \dots \dots (b)$$

in which (see I, p. 767 and 768)

$$\Omega' = \int p dv - pv - RT \sum n_1 \cdot \log \sum n_1,$$

or

$$\Omega' = \sum n_1 \cdot RT \log \frac{v-b}{\sum n_1} + \frac{a}{v} - pv, \dots \dots \dots (c)$$

when we make use of VAN DER WAALS' equation of state:

$$p = \frac{\sum n_1 \cdot RT}{v-b} - \frac{a}{v^2}.$$

So we find for $\frac{\partial \Omega'}{\partial n_1}$:

$$\frac{\partial \Omega'}{\partial n_1} = RT \log \frac{v-b}{\sum n_1} - RT - \frac{\sum n_1 \cdot RT}{v-b} b_1 + \frac{2a_1}{v},$$

because $\frac{\partial b}{\partial n_1} = b_1$ follows from $b = n_1 b_1 + n_2 b_2$, while from

$a = n_1^2 a_1 + 2 n_1 n_2 a_{12} + n_2^2 a_2$ is found $\frac{\partial a}{\partial n_1} = 2 n_1 a_1 + 2 n_2 a_{12} = (2 n_1 + n_2) a_1$, while a_{12} is evidently $= \frac{1}{2} a_1$ (cf. also I, p. 769).

Further $2 n_1 + n_2 = 2(1 - \beta) + 2\beta = 2$, hence finally $\frac{\partial a}{\partial n_1} = 2 a_1$.

The terms with $\frac{\partial v}{\partial n_1}$ all neutralize each other in consequence of the equation of state.

We can now write for the expression found:

$$\frac{\partial \Omega'}{\partial n_1} = RT \log \frac{v-b}{\Sigma n_1} - \frac{RT}{v-b} \left[v + n_2 (b_1 - b_2) \right] + \frac{2a_1}{v},$$

because $(v-b) + \Sigma n_1 \cdot b_1 = v - (n_1 b_1 + n_2 b_2) + (n_1 + n_2) b_1 = v + n_2 (b_1 - b_2)$.

If we still substitute $\frac{p + a/v^2}{\Sigma n_1}$ for $\frac{RT}{v-b}$, we get:

$$\frac{\partial \Omega'}{\partial n_1} = RT \log \frac{v-b}{\Sigma n_1} - \frac{p + a/v^2}{\Sigma n_1} v + \frac{2a_1}{v} - \frac{RT}{v-b} n_2 (b_1 - b_2),$$

or

$$\frac{\partial \Omega'}{\partial n_1} = RT \log \frac{v-b}{1+\beta} - \frac{pv}{1+\beta} + \frac{a}{v} \frac{1+2\beta}{1+\beta} - 2\beta RT \frac{b_1 - b_2}{v-b}, \quad (d)$$

as $a = a_1$ (see I, p. 769), $\Sigma n_1 = 1 + \beta$ and $n_2 = 2\beta$.

If $\beta = 0$, this passes into

$$\frac{\partial \Omega'}{\partial n_1} = RT \log (v-b) - pv + \frac{a}{v},$$

i.e. the expression (c) for Ω' , because then there is only one kind of molecules (viz. complex ones), and hence $\frac{\partial \Omega'}{\partial n_1}$ must be $= \Omega'$, when $\Sigma n_1 = 1 + \beta = 1$.

Now we find for the relation of equilibrium (a) in consequence of (b) and (d), as the function of the temperature C_1 disappears:

$$RT \log \frac{v'-b'}{v-b} \frac{1+\beta}{1+\beta'} - p \left(\frac{v'}{1+\beta'} - \frac{v}{1+\beta} \right) + a \left(\frac{1}{v'} \frac{1+2\beta'}{1+\beta'} - \frac{1}{v} \frac{1+2\beta}{1+\beta} \right) - \\ - 2 RT (b_1 - b_2) \left(\frac{\beta'}{v'-b'} - \frac{\beta}{v-b} \right) - RT \log \left(\frac{1-\beta'}{1+\beta'} \frac{1+\beta}{1-\beta} \right) = 0,$$

because $c_1 = \frac{n_1}{\Sigma n_1} = \frac{1-\beta}{1+\beta}$. The accented quantities refer to the *solid*

phase. If we now substitute $\frac{v-b}{1+\beta}$ for $\frac{RT}{p + a/v^2}$, we find finally after division by RT :

$$\log \frac{p + a/v^2}{p + a'/v'^2} = \frac{p}{RT} \left(\frac{v'}{1+\beta'} - \frac{v}{1+\beta} \right) - \frac{a}{RT} \left(\frac{1}{v'} \frac{1+2\beta'}{1+\beta'} - \frac{1}{v} \frac{1+2\beta}{1+\beta} \right) + \\ + 2 (b_1 - b_2) \left(\frac{\beta'}{v'-b'} - \frac{\beta}{v-b} \right) + \log \left(\frac{1-\beta'}{1+\beta'} \frac{1+\beta}{1-\beta} \right) \quad (16)$$

[For the coexistence liquid-vapour, instead of liquid-solid, this relation would pass into

$$\log \frac{a/v^2}{p} = \frac{pv'}{(1+\beta')RT} + \frac{a/v}{RT} \frac{1+2\beta}{1+\beta} - 2\beta \frac{b_1-b_2}{v-b} + \log \left(\frac{1-\beta'}{1+\beta'} \frac{1+\beta}{1-\beta} \right)$$

for sufficiently low temperatures, when v (liquid) may be neglected by the side of v' (vapour), $\frac{1}{v'}$ by the side of $\frac{1}{v}$, and $\frac{1}{v'-b'}$ by the side of $\frac{1}{v-b}$, $p + a/v^2$ then being $= a/v^2$, and $p + a'/v'^2$ then being $= p$; or it may pass into

$$\log \frac{a/v^2}{p} = \frac{a/v}{RT} \frac{1+2\beta}{1+\beta} + \frac{v-(1+\beta)b_1}{v-b} + \log \left(\frac{1-\beta'}{1+\beta'} \frac{1+\beta}{1-\beta} \right),$$

$$\text{because } \frac{pv'}{(1+\beta')RT} = 1 \text{ and } 1 - 2\beta \frac{b_1-b_2}{v-b} = \frac{v-(1-\beta)b_1-2\beta b_2-2\beta(b_1-b_2)}{v-b} = \frac{v-(1+\beta)b_1}{v-b}.$$

If now moreover $\beta = 0$, $\beta' = 0$, so that we have to deal with a simple substance, this ($b = b_1$) becomes:

$$\log \frac{a/v^2}{p} = \frac{a/v}{RT} + 1,$$

VAN DER WAALS' well-known relation for the pressure of coexistence, as viz. a/v^2 may be expressed in p_c and a/v in T_c (see TEYLER, p. 36—37)].

14. Let us return to the coexistence liquid-solid. The formula (16) holding for this might also have been found from the relation:

$$p_0 = \frac{1}{v'-v} \int_v^{v'} p dv = \frac{1}{v'-v} \int_v^{v'} \left(\frac{(1+\beta)RT}{v-b} - \frac{a}{v^2} \right) dv,$$

in which now the quantity β must be assumed to be variable in the integration between v and v' . But this course would have been far more lengthy, because then we should also have had to make use of the relation of equilibrium (2) [see I, p. 770]. We have, however, convinced ourselves that the result, as might be expected, is identical with (16).

As v and v' may be eliminated by means of the equation of state, β and β' by means of the relation of equilibrium (2), the derived relation (16) is really the required relation $p = f(T)$. But unfortunately these eliminations cannot really be carried out, so that we have to restrict ourselves to deriving the value of the pressure of

coexistence p in the different points of the curve SM (see fig. 6 of the Plate) from the relation (16) in connection with (2) and the equation of state.

With regard to $T=0$, we have already found by another way in II (see p. 35), that then

$$(T=0) \quad p_0 = \frac{q_0}{-\Delta b} - \frac{a}{vv'} \quad . \quad . \quad . \quad . \quad (10)$$

For in the relation (2) on p. 26, viz.

$$\frac{\beta^2}{1-\beta^2} = \frac{eT^{\gamma+1}}{p + a/v^2} e^{\frac{(p + a/v^2)(-\Delta b) - q_0}{RT}},$$

β will always be $=1$ for $T=0$, when $(p + a/v^2)(-\Delta b) > q_0$ (portion FE of fig. 5 on the plate of III; v is then constantly $=2b_2$). For then the second member $=0 \times e^\infty = \infty$. If on the other hand $(p + a/v^2)(-\Delta b) < q_0$ (part DC , where v is constantly $=b_1$; and part CB , where v increases from b_1 to ∞), β will always be $=0$ in consequence of $0 \times e^{-\infty} = 0$.

Along the portion ED of the isotherm, where β changes from 1 to 0 with variable v , $(p + a/v^2)(-\Delta b) - q_0$ must necessarily be $=0$, for else β would have to be either $=1$ or $=0$ according to the above. It is however easy to see, that the mentioned quantity with respect to T must be of the order $RT \log \frac{\lambda}{T^{\gamma+1}}$, for then

$$\frac{\beta^2}{1-\beta^2} = \frac{eT^{\gamma+1}}{p + a/v^2} \frac{\lambda}{T^{\gamma+1}} = \frac{e\lambda}{p + a/v^2},$$

which now remains finite for $T=0$, and may yield different values of β for different values of v . In the second member we have

$$p + a/v^2 = \frac{q_0}{-\Delta b} \quad \text{along the mentioned part } ED, \text{ so that } p + a/v^2$$

has a constant value, and for every value of v corresponds a definite value of p . Formula (10) follows then immediately from

$$p_0 = \frac{1}{v' - v} \int_v^{v'} p dv. \quad \text{And as } \frac{p + a/v^2}{RT} = \frac{1 + \beta}{v - b}, \quad v - b \text{ will then be per-}$$

manently $=0$, hence $v = b = b_1 + \beta \Delta b$, so that β may be found

$$\text{from } \beta = \frac{b_1 - v}{-\Delta b}. \quad (\text{See also the 2nd footnote on p. 120 of III}). \text{ By com-}$$

parison of this latter expression for β with the above one the value of λ , left undetermined just now, might be easily found.

15. We now proceed to consider the expression for $\frac{dp}{dT} = \frac{\Delta E}{T\Delta V}$ more closely.

The general equation for ΔV may be found from

$$\Delta V = v - v' = (b - b') + [(v - b) - (v' - b')].$$

In this $b = b_1 + \beta \Delta b$, $b' = b_1 + \beta' \Delta b$, hence $b - b' = (\beta - \beta') \Delta b$, so that we get:

$$-\Delta V = (\beta - \beta')(-\Delta b) - RT \left[\frac{1+\beta}{p+a/v^2} - \frac{1+\beta'}{p+a/v'^2} \right]. \quad (17)$$

Now as $\beta - \beta'$ is always *positive* (we indicated the phase with the *slightest* value of β , i.e. the *solid* phase, by accented quantities), while $-\Delta b$ is supposed to be *positive*, $-\Delta V$ will have its *greatest positive* value at $T=0$, viz. $-\Delta b$. For then $\beta - \beta'$ has its maximum value $1-0$, and the term with RT , in which $\frac{1+\beta}{p+a/v^2} > \frac{1+\beta'}{p+a/v'^2}$, will be as small as possible.¹⁾

For ΔE we may write (see (12) on p. 36 of II):

$$\Delta E = (\beta - \beta')(q_0 + \gamma RT) + \left(p + \frac{a}{vv'}\right) \Delta V,$$

or after substitution of the value of ΔV found:

$$\Delta E = (\beta - \beta') \gamma RT + (\beta - \beta') \left\{ q_0 - \left(p + \frac{a}{vv'}\right)(-\Delta b) \right\} + \left\{ + RT \left(p + \frac{a}{vv'}\right) \left[\frac{1+\beta}{p+a/v^2} - \frac{1+\beta'}{p+a/v'^2} \right] \right\}. \quad (18)$$

Now we saw above that $q_0 - \left(p + \frac{a}{vv'}\right)(-\Delta b)$, i.e. $q_0 - \left(p_0 + \frac{a}{v_0^2}\right)(-\Delta b)$, when p_0 is the pressure of coexistence at $T=0$, and v_0 is the "third" volume on the part ED (cf. also II, p. 35—36), is of the order

$$-(RT \log \lambda - (\gamma + 1) RT \log T),$$

i.e. of the order

$$\alpha T + \beta T \log T,$$

so that the above expression for ΔE must be of the order

$$\alpha' T + \beta T \log T = T(\alpha' + \beta \log T)$$

in the neighbourhood of $T=0$. So it follows from this that for $T=0$ also $\Delta E=0$; that for $T>0$ ΔE becomes at first *negative*

¹⁾ For in practice v and v' will differ very little, whereas β will mostly be considerably greater than β' (cf. also II, p. 39 footnote, where we demonstrated on the same ground that $v - b$ is always $> v' - b'$).

(for $\frac{d(\Delta E)}{dT} = (\alpha' + \beta) + \beta \log T$, which has the value $-\infty$ for $T=0$, as β is always positive); then reaches a *maximum* negative value (evidently when $\log T = -\frac{\alpha'+\beta}{\beta}$), increases again for higher values of T , becomes again $=0$ (when $\log T = -\frac{\alpha'}{\beta}$), and then remains always *positive*, and that increasing, because the increase of T and that of $q_0 - \left(p + \frac{a}{vv'}\right)(-\Delta b)$ will exceed the decrease of $\beta - \beta'$ in consequence of the continual decrease of the pressure of coexistence p .

In the expression

$$\frac{dp}{dT} = -\frac{\Delta E}{T(-\Delta V)}$$

$\frac{\Delta E}{T}$ will now be of the order $\alpha' + \beta \log T$ in the neighbourhood of $T=0$, so that then $-\frac{dp}{dT}$ is also of the order $\alpha' + \beta \log T$, because $-\Delta V$ remains finite. In other words: $\frac{dp}{dT}$ is $= +\infty$ for $T=0$; becomes $=0$ for $\log T = -\frac{\alpha'}{\beta}$, where ΔE becomes $=0$ for the second time (see above), and will then become *negative* and continue to *decrease*, because past the minimum of ΔE (for $\log T = -\frac{\alpha'+\beta}{\beta}$) ΔE continues to increase (see above), while we have already seen that $-\Delta V$ is a quantity *decreasing* with T .

So this course of $\frac{dp}{dT}$ gives for the line SM (coexistence liquid-solid) for *negative* values of Δb and ΔV a course as represented in Fig. 6 of the plate. (S is the triple-point). Hence the line SMN will *touch* the pressure axis in the point N ($T=0$), because there $\frac{dp}{dT} = \infty$.¹⁾

¹⁾ Disregarding the logarithmical order of ΔE , it has been erroneously derived in II, p. 36 [formule (12^a) and (13)] that the limiting value of ΔE for $T=0$ would be γRT , and therefore that of $\frac{dp}{dT}$ would have been given by $-\frac{\gamma R}{-\Delta b}$.

In the point S $\frac{dp}{dT}$ can even become *positive*, viz. when $-\Delta V$ becomes negative. This is e.g. the case when $-\Delta b$ has only a *slight* positive value, so that in (17) the term with $RT \left[\frac{1+\beta}{p+a/v^2} - \frac{1+\beta'}{p+a/v'^2} \right]$ begins to prevail for higher values of T ; in other words: when the sign of $v-v'$ is no longer only given by the sign of $b-b'$. In this case the line SM runs as indicated in fig. 7; i.e. with a vertical tangent in A , where $-\Delta V$ changes from positive to negative. Of course this point A may lie at very high pressure, so that it seems that the line SM *continues* to run to the right (which will of course only be the case for Δb positive).

16. It follows from the expression (10) of II p. 35, viz.

$$(T=0) \quad p_0 = \frac{q_0}{-\Delta b} - \frac{a}{vv'},$$

which we have already discussed there, that for *small* values of q_0 p_0 (the part ON at $T=0$) may become even 0 and negative. We shall then have a course as indicated in the figures 8—11.

The solid region contracts more and more, when p_0 decreases. At the same time the triple point S will move more and more to the absolute zero point 0.

As soon as p_0 has become negative (fig. 9), there appear necessarily two triple points S and S' , as the *realisable* pressure of coexistence remains, of course, positive. So with sufficient lowering of the temperature (the pressure remaining between that of M and S), we get first into the solid region, but finally again into the liquid region.

The possibility of such a course has already been suggested by TAMMANN (see inter alia BAKHUIS ROOZEBOOM, "die heterogenen Gleichgewichte" I p. 83, fig. 9) — with this important difference however, that TAMMANN supposes, besides a vertical tangent in A (see our fig. 7) and a horizontal one in M , another vertical tangent in A' and a horizontal one in M' (see fig. 12). Such a course, however, is

so a finite negative value; whereas in reality the last limiting value is $=+\infty$. But this error has had no further influence on what follows, as (12^a) and (13) have no more been used.

That at first the value of p itself at $T=0$ is *increasing*, appears from

$$q_0 - \left(p + \frac{a}{vv'} \right) (-\Delta b) = \alpha T + \beta T \log T,$$

which is decreasing for $T=0$, while vv' then remains unchanged.

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impossible according to our above theoretical considerations, as for $T=0$ *always* a pressure of coexistence exists (positive or negative). The grounds on which TAMMANN thinks such a course possible, are therefore theoretically not to be justified — as far as the points A' and M' are concerned.

Therefore BAKHUIS ROOZEBOOM has substituted the “half” egg for the “whole” egg of TAMMANN (see loc. cit. p. 93, fig. 10); but such a course (see fig. 13 of the plate) too is incompatible with theory.

BAKHUIS ROOZEBOOM tried to explain with this diagram why in many cases liquids do not *crystallise*, so that with lowering of the temperature a continuous transition would take place from the liquid into the amorphous glassy state, without this latter being metastable.

But this phenomenon is also explained by our theory. For with sufficiently low value of q_0 , p_0 becomes smaller and smaller, and even with comparatively very low pressures the solid region (see fig. 9, upper arrow) will no longer be reached. Finally the solid region will quite descend below the line OK and afterwards below the axis $p=0$ (see fig. 10 and 11), and we have a continuous liquid region — viz. from the moment that the line NM touches the line $OS'SMK$ (fig. 10), in which then S' and S will coincide.

Apart from the not accurately indicated course of the line SM past the point M , TAMMANN's figure is therefore closer to the probable truth (indicated by our fig. 9) than BAKHUIS ROOZEBOOM's figure with two pressures of coexistence in B and C at $T=0$. In the latter's diagram (fig. 13) the solid state might sometimes be reached by *increase* of pressure; with us, however (fig. 9), only by *decrease* of pressure.

The *absence* of the solid state can now be ascribed to *four* causes.

1. The liquid mass is already so viscous *before* the melting point (lying on the line SM) is reached, that it passes into the amorphous glassy state. In consequence of this the velocity of crystallisation is so slight, when the melting point is reached, that no crystallisation takes place, at least not immediately. Prof. JAEGER writes me that in such cases sometimes *after a very long time* devitrification takes place. So in this case we can do nothing but wait.

2. The melting point *is* reached in liquid state, but the pressure (e.g. that of one atmosphere), is *too high* (fig. 9, upper arrow). In this case we might try slowly to cool the liquid in a closed glass tube (so that at first it is *quite* filled with the liquid). The liquid is

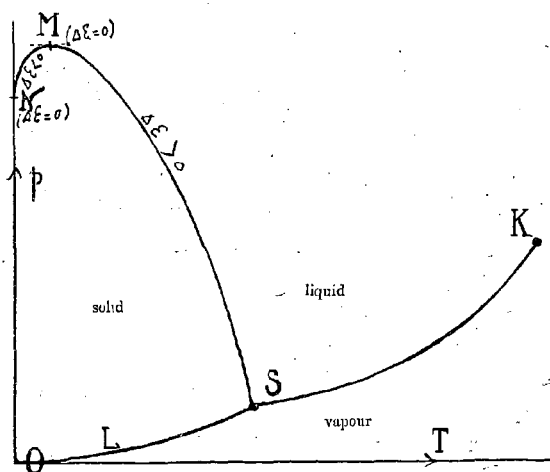


Fig. 6

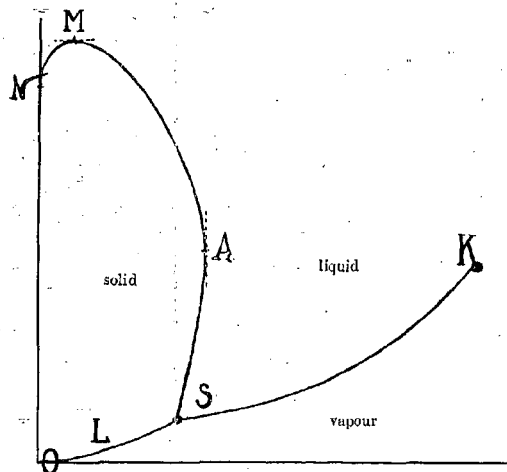


Fig. 7

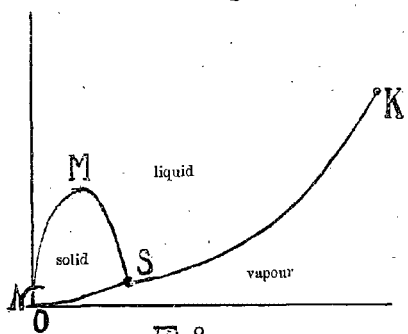


Fig. 8.
 $p_0 = \frac{a}{v_0 v_0'} (-\Delta b); p_0 = 0.$

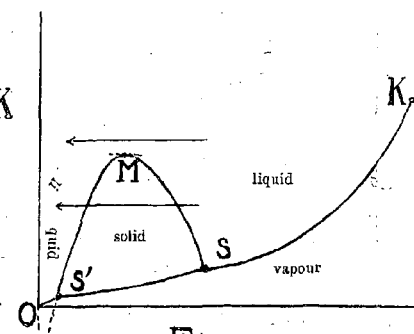


Fig. 9.
 $p_0 < \frac{a}{v_0 v_0'} (-\Delta b); p_0 < 0.$

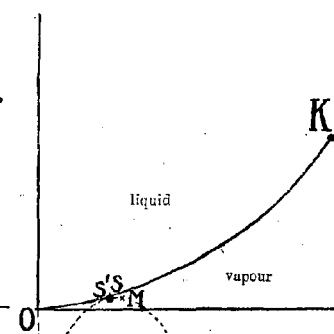


Fig. 10.

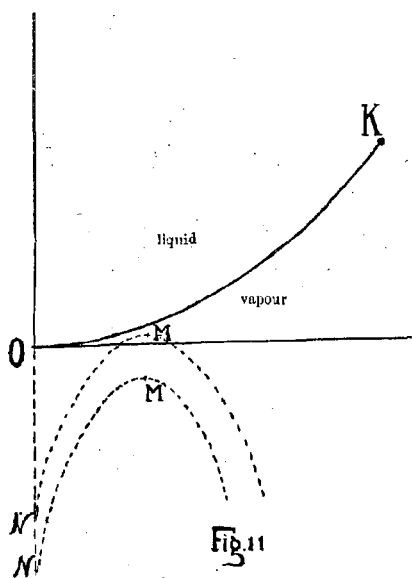


Fig. 11

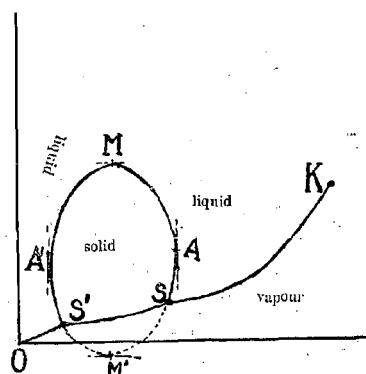


Fig. 12.

(TAMMANN.)

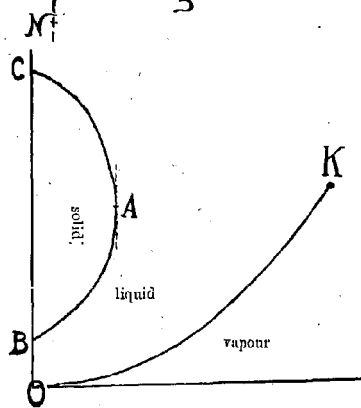


Fig. 13.

(BAKHUIS ROOZEBOOM.)

then continually under the pressure of the saturated vapour, so that we reach the point *S* along the line *KS*.¹⁾

3. The cooling has not been continued sufficiently long. For in cases as in fig. 9 the triple point *S* lies mostly at very low temperatures. Then, of course, only the cooling must be continued. It is however to be feared then, that the case 1 occurs before the line *SM* is reached.

4. There is no crystallized state (fig. 10 and 11). Then we may wait very long before the amorphous glassy mass crystallizes.

(*To be continued*).

Geology. — "*On oceanic deep-sea deposits of Central-Borneo*". By Prof. G. A. F. MOLENGRAAFF.

In the year 1894 I discovered in the basin of the Upper Kapoewas in Western Borneo²⁾ cherts and hornstones, consisting almost entirely of tests of Radiolaria, which I described as deep-sea deposits. Such rocks are also known as Radiolarite.

The Radiolaria from these deposits were examined by HINDE³⁾ and in consequence the age of these rocks was determined as pre-cretaceous, probably as jurassic.

The formation, of which these Radiolarites form part, I named the Danau-formation, after the large danaus or lakes of Western Borneo, where this formation is well-developed and was first observed by me. The Danau-formation there occupies a strip of country of an average breadth of 60—70 K.M. which is bordered on the north side by older formations, namely of the old-slate-formation, while on the south side it disappears under younger tertiary sandstones and volcanic products. The whole formation is strongly folded with an east-west strike, and forms part of the Upper Kapoewas mountain range.

From the lake district I could follow this formation eastward as far as the watershed between the Upper Kapoewas and the Upper

¹⁾ Might it not be possible to try to make some of the many substances mentioned to me by Mr. JAEGER crystallise as e. g. several esters of organic acids, amber-acid-nitril, and others?

²⁾ G. A. F. MOLENGRAAFF. Geological explorations in Central Borneo. p p. 123 & 414, Leiden 1902.

³⁾ G. J. HINDE, ibidem, Appendix I.