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genus, directly intermediate between *Polyporandra* BECC. and *Natsiatum* BUCHAN. Because the material is so incomplete, I have, however, thought it advisable to refrain even from proposing a new sub-genus and to assign to this species a place in the genus *Polyporandra*.

In the Herbarium of the Royal Botanic Gardens at Kew I last year compared authentic specimens of the only hitherto described species of *Polyporandra* (*P. scandens* BECCARI and *P. Hansemanni* ENGLER) with JUNGHUHN'S unicum of the Leiden Herbarium. In so doing I have become convinced that *Polyporandra scandens* and *Hansemanni* are very closely related but that, as was indicated above, our species (*Polyporandra Junghuhnii*) is sharply marked off from these specifically.

In conclusion I wish to tender my best thanks to the Director of the Royal Botanic Gardens in Kew, for the facilities given me for the comparison of the above-mentioned authentic specimens of BECCARI and of ENGLER.

Leiden, February 26th, 1909.

Physics. — "On the solid state". By Mr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of February 27, 1909).

1. In a recently published paper ¹⁾ I treated the complete theory of association, not only for gases and vapours, but also for liquids.

If we assume that only two simple molecules combine to a double molecule, the formula:

$$\frac{\beta^2}{1-\beta^2} = \frac{cT^{\nu+1} e^{-\frac{q_0 + (p + \frac{a}{c^2}) \Delta b}{RT}}}{p + \frac{a}{c^2}}, \dots \dots \dots (\alpha)$$

holds universally, in which c is a constant to be determined, and further:

$$\gamma = \frac{-k_1 + 2k_2}{R} ; \quad \Delta b = -b_1 + 2b_2.$$

So the quantity γR is the change of the specific heat for infinitely great constant volume, when 1 Gr. mol. of double molecules passes into 2 Gr. mol. of single molecules, while Δb is the change of the volume of the molecules in this transition. The quantity $q_0 = -(e_1)_0 + 2(e_2)_0$ repre-

¹⁾ In the *Arch. Tejler* (2) T. 11, Troisième partie, p. 235-331 (1909).

sents the absorption of heat for $T = 0$ taking place in this transition, and in the first member is β the degree of dissociation of the double molecules.

Besides various other things I demonstrated that the known discrepancies between the experimental critical data and those derived from VAN DER WAALS' equation of state in its usual form can be accounted for by the assumption of an association, which would even be still noticeable at the critical point.

I believe that this opinion was already expressed by VAN DER WAALS some years ago (1906)¹), and elaborated by VAN RIJ in his Thesis for the doctorate (1908); it was, however, demonstrated by me in the paper mentioned, that *quantitative* agreement can be obtained only when Δb is *not* $= 0$. Accordingly this quantity Δb plays an important part in my theory, which I drew up as early as 1902 on the occasion of a paper by the late Prof. BAKHUIS ROOZEBOOM.²)

But it is not about the above matters, however important, that I intend to speak now. I may be allowed to return to what I said on p. 259 of my paper in the Arch. Teyler (p. 25 of the reprint), namely that the isotherms — if Δb is not $= 0$ — present very "remarkable particularities" in the neighbourhood of $v = b$. (See fig. 1 of the plate).

These particularities now consist in this, that the isotherms, [for Δb positive only below a certain limiting temperature (critical temperature)] after having first risen to comparatively high pressures in the neighbourhood of $v = b$, bend back again as far as in the region of low (even negative) pressures, after which they rapidly ascend again for the second time to the highest pressures. We shall namely see that if e. g. Δb is positive, the degree of dissociation β of the double molecules approaches rapidly to 0 in the neighbourhood of $v = b = b_1 + \beta \Delta b$ in consequence of the relation (a), which causes $v - b$, after having first greatly decreased, to increase again. In consequence of this the pressure will decrease, and it will only increase again when $v - b$ begins to diminish again in the neighbourhood of the value $\beta = 0$. If Δb is negative, β will draw near to the limiting value 1, and we shall evidently see the same course appear in the values of $v - b$ and p .

¹) In an address delivered in the Meeting of this Academy of Jan. 1906, which address has unfortunately never been printed, so that only the fact and the subject of the address are known to me. (Cf. also the Thesis for the Doctorate of Dr. VAN RIJ on "Schijnassociatie etc", p. 3 (1908).

²) "Equilibria of phases in the system acetaldehyde + paraldehyde etc." (These Proc. Vol. XI, p. 283). Compare also VAN DER WAALS; "Some observations etc, These Proc. Vol. XI, p. 303.

It is clear that this may cause a new phase to appear, and that besides equilibrium between the vapour phase and the liquid phase as in the ordinary theory of VAN DER WAALS, under particular circumstances equilibrium may occur between the vapour phase and the third phase, or between the liquid phase and the new phase.

This phase, the molecular volume of which is somewhat less for positive Δb than that of the liquid phase, and for negative Δb somewhat larger, cannot be anything but a *solid phase* (amorphous or crystalline), which distinguishes itself from the liquid one in this, that the degree of dissociation of the double molecules (see § 3) is found in the neighbourhood of 0, so that the molecules are for the greater part in the state of *double molecules*; in the liquid state, however, this degree of dissociation can lie between the values 1 and almost 0, depending on whether we have to deal with so-called non-associating or with strongly associating liquids.

It is self-evident that formation of triple or multiple molecules is not excluded in this, but for the sake of simplicity I shall only work out the theory for partially dissociated double molecules in the following pages. The phenomena will not show any quantitative change by the occurrence of multiple molecules.

2. Before proceeding to a fuller discussion of the above formula (α), we shall first briefly repeat its derivation, and also set forth the influence of pressure and temperature on the equilibrium¹⁾.

In the condition of equilibrium:

$$-\mu_1 + 2\mu_2 = 0, \dots \dots \dots (1)$$

in which $\mu_1 = \frac{\partial \xi}{\partial n_1}$ and $\mu_2 = \frac{\partial \xi}{\partial n_2}$ represent the molecular thermodynamic potentials resp. of the double and of the simple molecules, we must substitute the well-known values for μ_1 and μ_2 .

Now:

$$\left. \begin{aligned} \mu_1 &= C_1 - \frac{\partial}{\partial n_1} [\Omega - RT \sum n_i \cdot \log \sum n_i] + RT \log c_1 \\ \mu_2 &= C_2 - \frac{\partial}{\partial n_2} [\Omega - RT \sum n_i \cdot \log \sum n_i] + RT \log c_2 \end{aligned} \right\}$$

in which the functions of the temperature C_1 and C_2 are given by:

$$\left. \begin{aligned} C_1 &= -k_1 T (\log T - 1) + [(e_1)_0 - T(s_1)_0] \\ C_2 &= -k_2 T (\log T - 1) + [(e_2)_0 - T(s_2)_0] \end{aligned} \right\}$$

while

¹⁾ Cf. Arch. Teyler, l.c.

$$\Omega = \int p dv - pv; \quad c_1 = \frac{n_1}{\Sigma n_1}; \quad c_2 = \frac{n_2}{\Sigma n_1}.$$

Hence substitution in (1) gives:

$$(-C_1 + 2C_2) - \left[-\frac{\partial \Omega'}{\partial n_1} + 2 \frac{\partial \Omega'}{\partial n_2} \right] + RT(-\log c_1 + 2 \log c_2) = 0,$$

when $\Omega' = \Omega - RT \Sigma n_1 \cdot \log \Sigma n_1$.

If β is the degree of dissociation of the double molecules, we have:

$$\frac{\partial \Omega'}{\partial \beta} = \frac{\partial \Omega'}{\partial n_1} \frac{dn_1}{d\beta} + \frac{\partial \Omega'}{\partial n_2} \frac{dn_2}{d\beta} = -\frac{\partial \Omega'}{\partial n_1} + 2 \frac{\partial \Omega'}{\partial n_2},$$

because $n_1 = 1 - \beta$, $n_2 = 2\beta$, so that we may write:

$$(-C_1 + 2C_2) - \frac{\partial \Omega'}{\partial \beta} + RT \log \frac{c_2^2}{c_1} = 0.$$

or as:

$$c_1 = \frac{1-\beta}{1+\beta}; \quad c_2 = \frac{2\beta}{1+\beta},$$

also:

$$\log \frac{4\beta^2}{1-\beta^2} = \frac{(C_1 - 2C_2) + \frac{\partial \Omega'}{\partial \beta}}{RT} \dots \dots \dots (a)$$

So we must determine the value of $\frac{\partial \Omega'}{\partial \beta}$. From:

$$p = \frac{(1 + \beta) RT}{v - b} - \frac{a}{v^2}$$

follows:

$$\int p dv = (1 + \beta) RT \log (v - b) + \frac{a}{v}, ^1)$$

so that we find for Ω' ($\Sigma n_1 = 1 + \beta$):

¹⁾ In this integration the quantity β must namely be kept constant, because an eventual *equilibrium* between the components exerts no influence on the determination of the values of Ω' , $\frac{\partial \Omega'}{\partial n_1}$ and $\frac{\partial \Omega'}{\partial n_2}$ for the two components. In the calculation of the thermodynamical potentials of the different components of an arbitrary mixture we have namely not to take account of a later eventual occurrence of an equilibrium. Thus we calculate here μ_1 and μ_2 quite independently, and simply introduce for the equilibrium the additional condition $-\mu_1 + 2\mu_2 = 0$. So we must imagine the integration $\int p dv$ for a *perfectly arbitrary* ratio of mixing β , which quantity β does not become the degree of dissociation of equilibrium until *after* the introduction of the condition $\mu_1 = 2\mu_2$. (see also Arch. Teyler p. 4).

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$$\Omega' = (1 + \beta) RT \log \frac{v-b}{1+\beta} + \frac{a}{v} - pv,$$

hence (a independent of β , see further below):

$$\frac{\partial \Omega'}{\partial \beta} = RT \log \frac{v-b}{1+\beta} - RT + \frac{(1+\beta) RT}{v-b} \left(\frac{\partial v}{\partial \beta} - \frac{db}{d\beta} \right) - \frac{a}{v^2} \frac{\partial v}{\partial \beta} - p \frac{\partial v}{\partial \beta}.$$

But in consequence of the equation of state all the terms with $\frac{\partial v}{\partial \beta}$ disappear, hence we get:

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

when we represent $\frac{db}{d\beta} = -b_1 + 2b_2$ by Δb . For b we may namely write:

$$b = b_1(1 - \beta) + b_2 \cdot 2\beta = b_1 + \beta(-b_1 + 2b_2) = b_1 + \beta \Delta b.$$

For a may be written:

$$a = (1 - \beta)^2 a_1 + 2(1 - \beta) 2\beta \cdot a_{12} + 4\beta^2 a_2.$$

But in case of simple association evidently $a_2 = 1/4 a_1$, $a_{12} = 1/2 a_1$, so that:

$$a = (1 - \beta)^2 a_1 + 2(1 - \beta) \beta \cdot a_1 + \beta^2 a_1 = a_1,$$

independent of β .

For the relation (a) we may now write:

$$\log \frac{4\beta^2}{1-\beta^2} = \left[C_1 - 2C_2 + RT \log RT - RT \log \left(p + \frac{a}{v^2} \right) - RT - \left(p + \frac{a}{v^2} \right) \Delta b \right] : RT,$$

or after substitution of the values of C_1 and C_2 :

$$\log \frac{\beta^2}{1-\beta^2} = \left[T(\log T - 1)(-k_1 + 2k_2) - (-(e_1)_0 + 2(e_2)_0) + T(-(s_1)_0 + 2(s_2)_0) + RT \log R + RT \log T - RT - RT \log 4 - RT \log \left(p + \frac{a}{v^2} \right) - \left(p + \frac{a}{v^2} \right) \Delta b \right] : RT.$$

If we now put:

$$\left. \begin{aligned} -\frac{k_1 + 2k_2}{R} + \frac{-(s_1)_0 + 2(s_2)_0}{R} + \log R - 1 - \log 4 &= \log c \\ -\frac{k_1 + 2k_2}{R} &= \gamma; \quad -(e_1)_0 + 2(e_2)_0 = q_0 \end{aligned} \right\}$$

we get:

$$\log \frac{\beta^2}{1-\beta^2} = \log c + \gamma \log T - \frac{q_0}{RT} + \log T - \log \left(p + \frac{a}{v^2} \right) - \frac{p + a/v^2}{RT} \Delta b,$$

or finally:

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

being the most general equation for the binary dissociation in arbitrary state of aggregation. The term with Δb disappears in the gaseous state, for then $\frac{p + a/v^2}{RT} = \frac{1 + \beta}{v - b}$, so that then $\frac{\Delta b}{v - b} = \frac{\Delta b}{v}$ verges to 0.

But for liquids (and solid bodies), it is by no means allowed to neglect this term (as was nearly always done up to now). For it would be very accidental indeed, if $\Delta b = -b_1 + 2b_2 = 0$. It is just this term with Δb , which exerts a very great influence on the value of β , and is one of the main causes for the occurrence of the solid state.

For perfect gases $p + \frac{a}{v^2}$ may also be replaced by p , and (2) passes into GIBBS'S well-known formula for the binary gas dissociation, e.g. of N_2O_4 into $2NO_2$:

$$\frac{\beta^2}{1-\beta^2} = \frac{cT^{\gamma+1} e^{-\frac{q_0}{RT}}}{p}.$$

For the further discussion of the equation (2) we refer to the original Paper in the *Arch. Teyler*; we may only be permitted to make the following general remarks.

If we vary the *pressure* at constant temperature, the second member of (2) will approach to ∞ for $p = 0$ ($v = \infty$) in consequence of the denominator p , hence β to 1. So in the perfect gas state everything is in the state of simple molecules.

But for *high* pressures the behaviour will be of two kinds, depending on whether Δb is positive or negative. For Δb *positive*, i.e. when the volume of two simple molecules is greater than of one double molecule, the second member of (2) will evidently approach to 0, when p approaches to ∞ . For then this member becomes $= \frac{e^{-\infty}}{\infty} = 0$. The value of β then approaches also to 0, i.e. there is complete association for $p = \infty$. If, however, Δb is *negative*, so that the volume of the double molecules is larger, the limiting value becomes $\frac{e^{+\infty}}{\infty} = \infty$, and then β

approaches again to 1, after having passed through a minimum value at a certain pressure (i.e. a maximum association). In the *Arch. Teyler* (p. 9) I demonstrated that $\frac{\partial\beta}{\partial p}$ changes its sign in this case, when v has become $= 2(b_1 - b_2) = b_1 - \Delta b$. (Δv given by formula (8) on p. 8 loc. cit. is namely $= 0$ then).

With regard to the influence of the *temperature* for constant pressure, it is easy to see that for $T = \infty$ as well as for $p = 0$ the dissociation is complete ($\beta = 1$), because $\gamma + 1$ is always positive.

But for lower temperatures the behaviour will again be different, depending on whether $q_0 + \left(p + \frac{a}{b^2}\right) \Delta b$ (v approaches then b , so that a/b^2 may be substituted for a/v^2) is positive or negative. If this quantity is *positive* [where Δb can be as well $+$ as $-$ (q_0 is always positive)], the second member of (2) approaches 0 at $T = 0$, so also β approaches 0 (complete association). But if $q_0 + \left(p + \frac{a}{b^2}\right) \Delta b$ is negative (which is only possible for Δb negative), β becomes again $= 1$ for $T = 0$, so that then a minimum value of the dissociation (maximum association) is passed through. I showed on p. 16 of the *Arch. Teyler* that $\frac{\partial\beta}{\partial T}$ changes its sign, when (see also p. 15 loc. cit.) $q = q_0 + \gamma RT + \left(p + \frac{a}{v^2}\right) \Delta v = 0$. The value of T for this minimum will depend on the pressure.

As for $\beta = 0$, $b = b_1 + \beta \Delta b$ approaches to b_1 , while for $\beta = 1$ the limiting value of b will be $2b_2$, we may also say that for $q_0 + \left(p + \frac{a}{b_1^2}\right) \Delta b$ positive β approaches to 0 at $T = 0$, while for $q_0 + \left(p + \frac{a}{4b_2^2}\right) \Delta b$ negative β will approach to 1 at $T = 0$.

For all this compare the figures 1 to 4 on p. 6 and p. 13 loc. cit.

3. Let us now examine the course of an isotherm in a p - v -diagram at a not too high temperature, and that first for the case that Δb is *negative*. Then, as we saw above, the value of β approaches to 1 for $p = \infty$, i.e. b to $2b_2$, the volume of the simple molecules. So this is smaller than b_1 .

The said course is (schematically) represented by fig. 1. (See the plate). Besides the usual maximum at B and the minimum at E of the ideal isotherm, according to the original equation of state of

VAN DER WAALS, another maximum at D and a minimum at C have now made their appearance. To A as vapour phase corresponds the coexisting *solid* phase A' . To P' as solid phase the coexisting liquid phase P'' . [cf. also the p - T -diagram of fig. 4 (I), where the line SM runs back in consequence of the fact that Δb is negative, which implies that also Δv is negative for the transition solid-liquid ($P'P''$). By approximation the quantity Δv is namely $= (\beta_l - \beta_s) \Delta b$, in which $\beta_{liq.}$ is always $> \beta_{sol.}$]. The pressure of coexistence at $P'P''$ will always be much greater than that at $A'A''$, when the temperature is considerably lower than that of the triple point S (see fig. 4). For not too low values of T we may also have a metastable coexistence gas-liquid QQ'' (cf. figs. 1 and 4). If the temperature is very low (as in the following calculation), β will draw near to 1 only for exceedingly high values of v , whereas for all values of v between A and D the value of β is practically $= 0$ (association is complete), as will appear from the following calculation. The minimum value of β , which was mentioned in § 2, then lies in the immediate neighbourhood of 0. Only between the points D and E does β increase rapidly from $\beta = (\pm) 0$ to $\beta = (\pm) 1$, and this in consequence of the rapid decrease from $v = (\pm) b_1$ to $v = (\pm) 2b_2$. From E to the highest pressures β remains then in the immediate neighbourhood of 1, and becomes exactly $= 1$ for $p = \infty$ ($v = 2b_2$). It is self-evident that for higher values of T the values of β for P' and P'' will approach each other more.

At the temperature of the triple point S the three transitions AA' , QQ'' (metastable), and $P'P''$ will coincide. There is only one pressure of coexistence (three-phase-pressure).

For temperatures above that of S (comp. fig. 2 and fig. 4 (II)) the coexistence QQ'' , which was first metastable, has become stable, whereas AA' has now become metastable, just as $P'P''$. (These last transitions, of course, at not too high values of T). Now only a liquid phase coexists with the vapour phase.

For higher temperatures the minimum at C and the maximum at D will draw nearer to each other, and they will finally coincide in an horizontal point of inflection C,D (comp. fig. 3 and fig. 4 (III)). From this moment we have, therefore, the original isotherm of VAN DER WAALS with the simple coexistence gas-liquid.

At last at still higher temperature (the critical temperature in K) also the last maximum (B) and minimum (E) will coincide.

How all this is modified when Δb is *positive*, and so the line SM runs to the right in fig. 4, will be easily seen by the reader. We shall revert to this in a following paper, and mention now only that

then (see fig. 1) $v = 2b_2$ lies on the right of $v = b_1$, and accordingly the solid phase not on the right but on the left of the liquid one. Not C and D , but D and E will then coincide in an horizontal point of inflection (critical point solid-liquid).

4. After the above digression we return again to the shape of the isotherm in fig. 1, and we shall carry out a simple computation to prove our statements. For this purpose we shall first modify the principal equations somewhat.

If we put:

$$\frac{p + a/v^2}{RT} (-\Delta b) = \varphi \quad ; \quad \frac{RT}{q_0} = \theta,$$

we can write equation (2) in the form:

$$\frac{\beta^2}{1-\beta^2} = \frac{cq_0^\gamma}{R^{\gamma+1}} (-\Delta b) \cdot \theta^\gamma e^{-1/\theta} \frac{e^\varphi}{\varphi},$$

i. e.

$$\frac{\beta^2}{1-\beta^2} = \lambda \theta^\gamma e^{-1/\theta} \frac{e^\varphi}{\varphi}, \dots \dots \dots (3)$$

when

$$\frac{cq_0^\gamma}{R^{\gamma+1}} (-\Delta b) = \lambda$$

is put.

For

$$p = \frac{(1+\beta) RT}{v-b} - \frac{a}{v^2}$$

may evidently be written:

$$p = \frac{RT}{(-\Delta b)} \varphi - \frac{a}{v^2}, \dots \dots \dots (4)$$

and the value of v can be calculated from:

$$v = b + (v-b) = b + \frac{1+\beta}{\varphi} (-\Delta b),$$

or as $b = b_1 + \beta \Delta b$, from:

$$v = b_1 - \left(\beta - \frac{1+\beta}{\varphi} \right) (-\Delta b) \dots \dots \dots (5)$$

So if we successively assume different values of φ for given values of $\lambda, \gamma, b_1, -\Delta b$ and $\theta (T)$, we may calculate for each of them the corresponding values of β, v and p .

If we assume:

$c = 2$ (Gr. Cal.); $q_0 = 3200$ (Gr. Cal.); $b_1 = 1$; $2b_2 = 1/2$; $a = 2700$, so that

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$$-\Delta b = -(b_1 + 2b_2) = 1/2,$$

and [with $R = 2$ (Gr. Kal.)]

$$\lambda = \frac{2 \times (3200)^{3/2}}{2^{3/2}} \times 1/2 = (1600)^{3/2} \times 1/2 = 64000 \times 1/2 = 32000$$

becomes; while for T is taken 9° (absolute), yielding:

$$\varphi = \frac{1}{36} \left(p + \frac{a}{v^2} \right); \quad \theta = \frac{9}{1600},$$

the equations (3), (4) and (5) become:

$$\left. \begin{aligned} \frac{\beta^2}{1-\beta^2} &= 32000 \times \left(\frac{9}{1600} \right)^{3/2} e^{-\frac{1600}{9}} \frac{e^{\varphi}}{\varphi} = \frac{27}{2} e^{-\frac{1600}{9}} \frac{e^{\varphi}}{\varphi} \\ v &= 1 - \frac{1}{2} \left(\beta - \frac{1+\beta}{\varphi} \right); \quad p = 36\varphi - \frac{2700}{v^2} \end{aligned} \right\} \quad (6)$$

For $\varphi = \infty$ we get evidently:

$$\beta = 1; \quad v = 1 - 1/2 \beta = 1/2 (= 2b_2); \quad p = \infty.$$

For $\varphi = 185$ we find:

$$\begin{aligned} \log^{10} \frac{\beta^2}{1-\beta^2} &= -76,077 + 0,4343 \varphi - \log^{10} \varphi \quad \dots \quad (6^a) \\ &= -76,077 + 80,343 - 2,267 = 1,999, \end{aligned}$$

because:

$$\log^{10} \frac{27}{2} - \frac{1600}{9} \times 0,43429 = 1,130 - 77,207 = -76,077,$$

in consequence of which:

$$\frac{\beta^2}{1-\beta^2} = 99,77; \quad \beta = 1 - \frac{1}{199,54}.$$

So between $\varphi = \infty$ and $\varphi = 185$ β is practically $= 1$.

So we find for v :

$$v = 1 - \frac{1}{2} \left(1 - \frac{1}{200} - \frac{2}{185} \right) = 1 - 0,492 = 0,508,$$

while:

$$p = 6660 - \frac{2700}{(0,508)^2} = 6660 - \frac{2700}{0,258} = -3800,$$

R being expressed in Gr. Cal. ($R = 2$) in the equation of state,

also pv and $\frac{a}{v}$ are expressed in caloric units, so that if v, b etc.

are given in cM^3 (per Gr. mol), the values of pv and $\frac{a}{v}$ in ergs

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are found by multiplication by $41,74 \times 10^6$. Then p and $\frac{a}{v^2}$ are expressed in dynes per c.M². But as 1 atm. = $1,01325 \times 10^6$ dynes per c.M²., we find the number of atmospheres of p and $\frac{a}{v^2}$ by multiplication of the found values by $\frac{41,73}{1,013} = 41,20$.

The found pressure which will lie in the neighbourhood of the point E in fig. 1, amounts therefore to $-3800 \times 41,20 = -156600$ atm., from which appears how enormous the distance is of the points D and E at such low temperatures. (At higher temperatures both the term $-76,08$ in the equation for β and the factor 36 in the equation for p will become considerably higher).

In a similar way, as above we can now calculate for

$\varphi = 180$:

$$\log^{10} \frac{\beta^2}{1-\beta^2} = -76,076 + 78,173 - 2,255 = -0,160$$

$$\frac{\beta^2}{1-\beta^2} = 0,692 \quad ; \quad \beta = 0,640$$

$$v = 1 - \frac{1}{2} \left(0,640 - \frac{1,640}{180} \right) = 1 - 0,315 = 0,685$$

$$p = 6480 - \frac{2700}{0,469} = 6480 - 5760 = 720.$$

$\varphi = 170$:

$$\log^{10} \frac{\beta^2}{1-\beta^2} = -76,077 + 73,829 - 2,230 = -4,478$$

$$\frac{\beta^2}{1-\beta^2} = 0,0000331 \quad ; \quad \beta = 0,00575$$

$$v = 1 - \frac{1}{2} \left(0,0058 - \frac{1,0058}{170} \right) = 1 + 0,0001 = 1,0001$$

$$p = 6120 - \frac{2700}{1,0002} = 6120 - 2700 = 3420.$$

$\varphi = 160$:

$$\log^{10} \frac{\beta^2}{1-\beta^2} = -76,077 + 69,486 - 2,204 = -8,795$$

$$\beta = 0$$

$$v = 1 + \frac{1}{320} = 1,003$$

$$p = 5760 - \frac{2700}{1,006} = 5760 - 2680 = 3080$$

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$\varphi = 100$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{200} = 1,005$$

$$p = 3600 - \frac{2700}{1,010} = 3600 - 2670 = 930.$$

$\varphi = 50$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{100} = 1,01$$

$$p = 1800 - \frac{2700}{1,020} = 1800 - 2650 = - 850.$$

$\varphi = 10$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{20} = 1,05$$

$$p = 360 - \frac{2700}{1,103} = 360 - 2450 = - 2090.$$

$\varphi = 1$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{2} = 1,5$$

$$p = 36 - \frac{2700}{2,25} = 36 - 1200 = - 1160$$

$\varphi = 0,1$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{0,2} = 6$$

$$p = 3,6 - \frac{2700}{36} = 3,6 - 75 = - 71.$$

$\varphi = 0,01$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{0,02} = 51$$

$$p = 0,36 - \frac{2700}{2601} = 0,36 - 1,04 = - 0,68.$$

$\varphi = 0,001$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{0,002} = 501$$

$$p = 0,036 - \frac{2700}{251000} = 0,036 - 0,011 = 0,025.$$

$\varphi = 10^{-74}$:

$$\log \frac{\beta^2}{1-\beta^2} = - 76,077 + 0 + 74 = - 2,077$$

$$\frac{\beta^2}{1-\beta^2} = 0,00838 \quad ; \quad \beta = 0,0911$$

$$v = 0,546 \times 10^{74} \quad ; \quad p = 36 \cdot 10^{-74}.$$

$\varphi = 0$:

$$\beta = 1 \quad ; \quad v = \infty \quad ; \quad p = 0.$$

With regard to the course of the values of β we see clearly from this calculation, that between the points $F(p = \infty)$ and $E(p = -4130)$ in fig. 1 β is practically = 1 ($\beta = 0,983$ in E). This is due to the fact that between $\varphi = \infty$ and $\varphi = 185$, $\log^{10} \frac{\beta^2}{1-\beta^2}$ in (6^a) has a comparatively high *positive* value (at $\varphi = 185$ still = 2), in consequence of the value of $0,4343 \varphi$, which is then $> -76,08$ (this value holds for $T = 9$), so that $\frac{\beta^2}{1-\beta^2}$ is large, and β will lie in the neighbourhood of 1 (for $\varphi = 185$ β is still as great as = $0,995$).

But between E and D , i. e. between $\varphi = 185$ and $\varphi = 170$, a *very rapid change* in the value of β takes place. The value of $0,4343 \varphi$ becomes then namely $< -76,08$, in consequence of which $\log^{10} \frac{\beta^2}{1-\beta^2}$ decreases from a positive value to a comparatively large *negative* one (for $\varphi = 170$ already = $-4,5$), so that β changes rapidly from 1 to 0. In the point D we have $\beta = 0,027$, while $\beta = 0,006$ for $\varphi = 170$. For $\varphi = 180$ at about $\frac{2}{3}$ of the distance between E and D , we have the intermediate value $0,64$.

So the entire change of β takes practically place between the points E and D . Past D β remains practically = 0, till at about $\varphi = 10^{-74}$, at an enormous value of v ($v = 0,55 \times 10^{74}$), the value of β gradually rises from 0 to 1. In equation (6^a) the term $-\log^{10} \varphi$ begins then to approach the term $-76,08$ in absolute value, and it exceeds this term for values of $\varphi < 10^{-76}$. For $\varphi = 10^{-74}$ β is already $0,09$, while for $\varphi = 0$ ($v = \infty$) β will have become = 1. So this transition takes place beyond the limits of the diagram (fig. 1) (for $T = 9$).

What was said above, gives a clear idea of the course of the values of β , and we see at the same time from it, that in the transition solid-liquid ($P'P''$) the value of β_{liquid} is practically = 1, and that of β_{solid} practically = 0. For the point P'' lies between E and D , and the point P' beyond D .

The corresponding values of p have been indicated everywhere in the figure, while those of v appear from the above calculation.

5. In connection with what was discussed before, we will finally give the calculation of the different maxima and minima in fig. 1, viz. of the points B, C, D and E .

From the equation of state:

$$p = \frac{(1 + \beta) RT}{v - b} - \frac{a}{v^2}$$

it is easy to derive for T constant (keeping in mind that $b = b_1 + \beta \Delta b$):¹⁾

$$\frac{dp}{dv} = - \frac{(1 - \beta) RT}{(v - b)^2} \left(1 - \Delta b \frac{\partial \beta}{\partial v} \right) + \frac{RT}{v - b} \frac{\partial \beta}{\partial v} + \frac{2a}{v^3},$$

i. e. with
$$\frac{(1 + \beta)(-\Delta b)}{v - b} = \varphi:$$

$$\frac{dp}{dv} = \frac{2a}{v^3} - \frac{(1 + \beta) RT}{(v - b)^2} \left[1 - (1 - \varphi) \frac{v - b}{1 + \beta} \frac{\partial \beta}{\partial v} \right].$$

But from the equation (2) for β , viz. in the form (written $\frac{(1 + \beta) RT}{v - b}$ for $p + \frac{a}{v^2}$):

$$\frac{\beta^2}{1 - \beta^2} = \frac{f(T)}{RT} \frac{v - b}{1 + \beta} e^{-\frac{(1 + \beta) \Delta b}{v - b}},$$

from which p has been eliminated, follows by logarithmical differentiation (T constant) after some reductions (see p. 36—37 loc.cit.)

$$\frac{v - b}{1 + \beta} \frac{\partial \beta}{\partial v} = \frac{1/2 \beta (1 - \beta) (1 - \varphi)}{1 + 1/2 \beta (1 - \beta) (1 - \varphi)^2}.$$

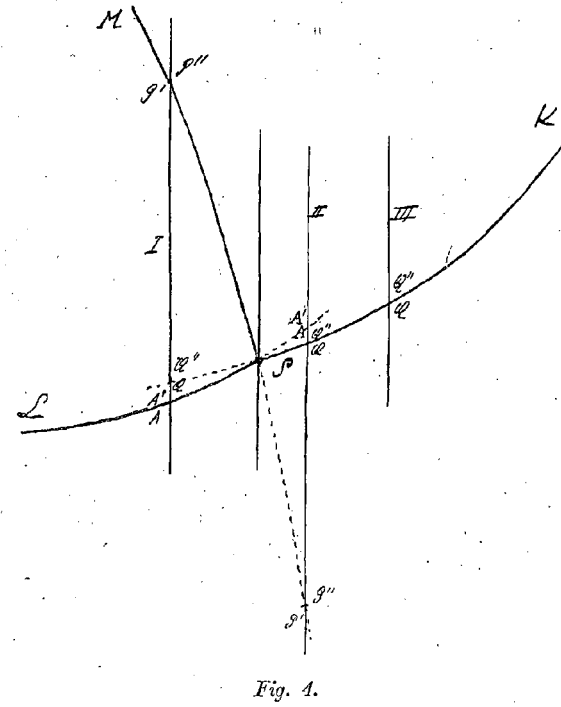
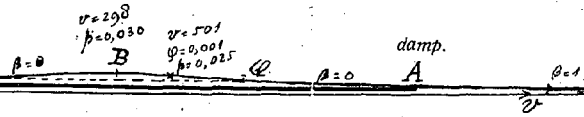
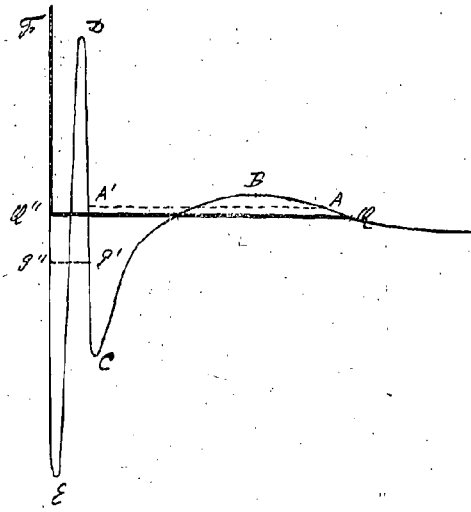
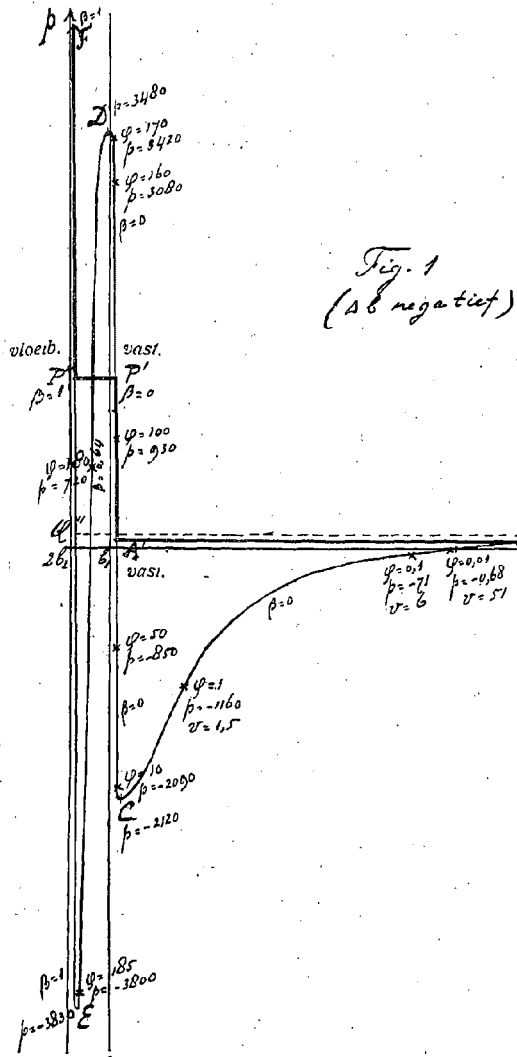
By substitution in the expression for $\frac{dp}{dv}$ obtained above we get now:

$$\frac{dp}{dv} = \frac{2a}{v^3} - \frac{(1 + \beta) RT}{(v - b)^2} \frac{1}{1 + 1/2 \beta (1 - \beta) (1 - \varphi)^2} \dots (7)$$

This expression passes into the ordinary one for $\beta = 0$ and 1. [It is true that for $\beta = 1$ we obtain $\frac{dp}{dv} = \frac{2a}{v^3} - \frac{2RT}{(v - b)^2}$, but a, v and b referring to double-molecular quantities, $a = 4a'$, $v = 2v'$, $b = 2b'$ will have to be substituted, in which the accentuated quantities now refer to single molecular quantities. We get then $\frac{dp}{dv'} = \frac{2a'}{v'^3} - \frac{RT}{(v' - b')^2}$, as we should get.]

Let us now first examine the points D and E (fig. 1). There $v - b$ is small, so φ large. In this we notice that the just introduced quantity φ is the same as our former quantity φ . For in (3) etc. $\frac{p + \frac{a'}{v'^2}}{RT} (-\Delta b) = \varphi$ was put, so also $\frac{(1 + \beta)(-\Delta b)}{v - b} = \varphi$. Now $\varphi = 185$

¹⁾ See also Arch. Teyler, l.c. p. 26—27.



for E and $\varphi = 170$ for D (see § 4), so that we may write $\frac{1}{2}\beta(1-\beta)\varphi^2$ instead of $1 + \frac{1}{2}\beta(1-\beta)(1-\varphi)^2$ — if namely the value of β and $1-\beta$ is not too small. It will presently appear that this is not the case.

So in the points D and E we have got by approximation:

$$\frac{2a}{v^3} = \frac{(1+\beta)RT}{(v-b)^2} \cdot \frac{1}{\frac{1}{2}\beta(1-\beta)\frac{(1+\beta)^2(-\Delta b)^2}{(v-b)^2}} = \frac{RT}{\frac{1}{2}\beta(1-\beta^2)(-\Delta b)^2}.$$

Now in D (see fig. 1) v is in the neighbourhood of b_1 , whereas in E the volume v is in the neighbourhood of $2b_2$; hence if we put $1-\beta$ and $1+\beta=1$ for D , where β is near 0; and $\beta=1$, $1+\beta=2$ for E , where β is near 1, we get by approximation ($R=2$)

$$\beta_D = \frac{2T}{\frac{a}{b_1^3}(-\Delta b)^2} ; \quad 1-\beta_E = \frac{T}{\frac{a}{(2b_2)^3}(-\Delta b)^2}.$$

So with $T=9$, $a=2700$, $b_1=1$, $2b_2=1/2$, $-\Delta b=1/2$ we find:

$$\beta_D = \frac{18}{2700 \times 1/4} = \frac{2}{75} = 0,027 ; \quad 1-\beta_E = \frac{9}{2700 \times 8 \times 1/4} = \frac{1}{600} = 0,0017.$$

So above at D we have neglected 1 by the side of circa $0,0133 \times 170^2 = 400$, and at E we have neglected 1 by the side of circa $0,00083 \times 185^2 = 28,5$; so that the above values of β_D and $1-\beta_E$ may be considered as permissible approximations.

It is now easy to calculate the pressure in the points D and E from the equation of state. With $\frac{(1+\beta)(-\Delta b)}{v-b} = \varphi$ the latter becomes (see equation (4) and (6)):

$$p = \frac{RT}{-\Delta b} \varphi - \frac{a}{v^2} = 36\varphi - \frac{2700}{v^2}.$$

Hence we find:

$$p_E = 6700 - 10530 = -3830,$$

as according to (6^a) $\varphi = 186$ and $v = 0,506$ corresponds to $\beta_E = 1 - \frac{1}{600}$.

And as $\varphi = 173$ and $v_D = 0,99$ corresponds to $\beta_D = 0,027$:

$$p_D = 6230 - 2750 = 3480.$$

As to the points B and C , for them $\beta = 0$ for $T = 9$, as we saw before. So there is simply:

$$\frac{2a}{v^3} = \frac{RT}{(v-b)^2},$$

(780)

i.e. with $b = b_1 = 1$:

$$\frac{v^3}{(v-1)^2} = 300,$$

yielding $v_B = 298$ and $v_C = 1,063$.

Hence from.

$$p = \frac{18}{v-1} - \frac{2700}{v^2}$$

we find:

$$p_B = 0,0606 - 0,0304 = 0,0302$$

$$p_C = 280 - 2400 = -2120.$$

So reviewing what has been said, we can account for the appearance of the different maxima and minima in the following way.

In the expression $p = \frac{RT}{v-b} - \frac{a}{v^2}$ the term $\frac{RT}{v-b}$ will increase more

rapidly than $\frac{a}{v^2}$ between the points A and B , in consequence of the decrease of v , so that p becomes larger. Between B and C , on the other hand, the increase of $\frac{a}{v^2}$ will predominate, so that p decreases.

But beyond C , when v comes near b , $\frac{RT}{v-b}$ will again increase more

than $\frac{a}{v^2}$, and the isotherm will now ascend very rapidly. It would proceed to $p = \infty$ (according to the original theory), but *in consequence of the abrupt change of the value of β between D and E from 0 into 1*, the value of a/v^2 will increase rapidly from a/v^2 to $a/4b^2$. For E , where this increase of β has ceased, $v - b$ will begin to decrease again from this moment, so that p can ascend indefinitely.

Hence, when only the *state of association* β of the molecules for small volumes is taken into consideration, in connection with the *variation of volume* Δb attending it, not only the liquid state, but also the *solid state* (crystallized or not) is quite controlled by VAN DER WAALS' equation of state.

Further particulars, referring to the case Δb positive, to the formation of multiple complexes, to different modifications of the solid state, to the ratio $\frac{T_0}{T_c}$, where T_0 is the triple-point temperature, and T_c the ordinary critical temperature, etc. etc, will be discussed in a subsequent paper.