

*Citation:*

Johannes Diderik van der Waals, Quasi-association or molecule-complexes. II, in:  
KNAW, Proceedings, 13 I, 1910, Amsterdam, 1910, pp. 494-506

Physics. — “*Quasi-association or molecule-complexes.*” II. By Prof.  
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(Communicated in the meeting of October 29, 1910).

IX. *A substance in quasi-association considered as a binary system.*

When a substance is in a state of quasi-association, it consists of molecules with different properties, viz. simple ones and complex ones. We have simplified in so far that we have only supposed two kinds of molecules, simple ones and  $n$ -fold ones, though it is probable, especially when  $n$  is great, that it may have a variable value. In this case  $n$  must be considered as a mean value. Of the complex molecules we have to consider the volume  $n$  times larger than that of the simple molecules, and we have come to the conclusion that the attraction which exists between the molecules has a twofold effect then. First of all it brings about the aggregation to molecule-complexes, and for another part, but then to a diminished amount, it remains present as molecular pressure. For that molecular pressure  $a$  is diminished to  $a\left(1 - \frac{x}{2}\right)^2$ . That this aggregation is to be expected when the molecular attraction diminishes exceedingly rapidly, and only makes itself felt at distances which are comparable with the mean distance of the molecules, had already been foreseen by BOLZMANN, as DEBYE remarks. (Ann. der Physik 1910). But then it should also be accepted, in my opinion, that this is accompanied by a decrease of the molecular pressure.

That such an aggregation, called by me quasi-association, exists, I derived in the preceding first part (These Proc. June 1910) from the differences which the experiment presents with every equation of state for which such an association is not assumed. For it was demonstrated there that the assumption of  $a$  as temperature function is not to be reconciled with the course of the existing differences. It has also been shown at length that the assumption of  $b$  as temperature function cannot account for the existing differences either, though I referred for the proof to VAN RIJ's thesis for the doctorate. That also other suppositions concerning the value of the molecular pressure are insufficient to do so, I have stated, though I have omitted the proof. And to increase the confidence in the existence of this quasi-association I will prove this here first of all. To a value of the molecular pressure of  $\frac{a}{v^\mu}$  corresponds a value of the

energy of  $-\frac{1}{\mu-1} \frac{a}{v^{\mu-1}}$ , and a value of

$$\left(\frac{T}{p} \frac{dp}{dT} - 1\right) p = \frac{1}{\mu-1} \frac{\frac{a}{v_1^{\mu-1}} - \frac{a}{v_2^{\mu-1}}}{v_2 - v_1}, \text{ or putting } \frac{1}{v} = \varrho:$$

$$\left(\frac{T}{p} \frac{dp}{dT} - 1\right) \frac{pv_1 v_2}{a} = \frac{1}{\mu-1} \frac{\varrho_1^{\mu-1} - \varrho_2^{\mu-1}}{\varrho_1 - \varrho_2},$$

while

$$\left(\frac{T}{p} \frac{dp}{dT} - 1\right)_{kr} \frac{pkv_k^2}{a} = \varrho_k^{\mu-2}.$$

By division of the two last equations by each other we find:

$$1 + \varphi = 1 + \sqrt{1-m} - \frac{1-m}{2} = \frac{1}{\mu-1} \frac{\left(\frac{\varrho_1}{\varrho_k}\right)^{\mu-1} - \left(\frac{\varrho_2}{\varrho_k}\right)^{\mu-1}}{\left(\frac{\varrho_1}{\varrho_k}\right) - \left(\frac{\varrho_2}{\varrho_k}\right)}$$

The last term has a value of  $= 1$  for  $\mu = 2$ , a value of  $\frac{1}{2} \left\{ \left(\frac{\varrho_1}{\varrho_k} + \frac{\varrho_2}{\varrho_k}\right) \right\}$  for  $\mu = 3$ , or a value of  $1 + \gamma(1-m)$  as  $\frac{\varrho_1 + \varrho_2}{\varrho_k} = 2 \{1 + \gamma(1-m)\}$ .

So the rapid increase of the quantity  $\varphi$ , which already amounts to 0,1 for  $1-m=0,01$  according to the observations, is not even explained by  $\mu = 3$ , but would then amount to no more than 0,008.

A value of  $\mu = \frac{7}{3}$ , which was put by KLEEMAN (Phil. Mag. Oct. 1910) would even be less adequate to do so.

For a value of  $\mu$  between 2 and 3,  $\varphi$  also has a value between 0 and  $\gamma(1-m)$ . We can namely show that for equal value of  $1-m$ , the quantity  $\varphi$  increases with  $\mu$ .

Putting  $\frac{\varrho_1}{\varrho_k} = 1 + \Delta_1$  and  $\frac{\varrho_2}{\varrho_k} = 1 - \Delta_2$ , we have namely:

$$1 + \varphi = \frac{1}{\mu-1} \frac{(1 + \Delta_1)^{\mu-1} - (1 - \Delta_2)^{\mu-1}}{\Delta_1 + \Delta_2},$$

and from this follows:

$$\frac{d\varphi}{(1+\varphi)d\mu} = -\frac{1}{(\mu-1)^2} + \frac{(1+\Delta_1)^{\mu-1} N_{ep} \log(1+\Delta_1) - (1-\Delta_2)^{\mu-1} N_{ep} \log(1-\Delta_2)}{(1+\Delta_1)^{\mu-1} - (1-\Delta_2)^{\mu-1}}.$$

If we confine ourselves to small values of  $1-m$ , and so also to small values of  $\Delta_1$  and  $\Delta_2$ , we find:

$$\frac{d\varphi}{(1+\varphi)d\mu} = -\frac{1}{(\mu-1)^2} + \frac{1}{\mu-1} = \frac{\mu-2}{(\mu-1)^2}.$$

Moreover, if we confine ourselves to small values of  $\Delta_1$  and  $\Delta_2$  we find for  $1 + \varphi$  the value:

$$\frac{(\mu-1)(\Delta_1 + \Delta_2) + \frac{(\mu-1)(\mu-2)}{1 \cdot 2}(\Delta_1^2 - \Delta_2^2)}{(\mu-1)(\Delta_1 + \Delta_2)}$$

or

$$1 + \varphi = 1 + \frac{\mu-2}{1 \cdot 2}(\Delta_1 - \Delta_2) = 1 + (\mu-2)\gamma(1-m).$$

So  $\varphi$  would be  $= \frac{1}{3}\gamma(1-m)$  for  $\mu = \frac{7}{3}$ , so much too small, at least for very small value of  $1-m$ .

So we come to the conclusion, that the observations in the neighbourhood of the critical point and a fortiori at lower temperatures and greater density lead to the assumption of quasi-association — and if we then take a single value for  $n$  by way of simplification, we have a binary system.

If we now determine the value of  $\psi$  at given temperature for all possible values of  $x$ , representing the fraction present as simple molecules by  $1-x$ , such a value of  $\psi$  as function of  $x$  and  $v$  represents a surface. It is true that on account of the possibility of the transition of the substance from the simple to the  $n$ -fold molecular state by no means all the points of such a surface represent states which can really occur. A second equation holds for the determination of those points of the  $\psi$ -surface which represent really occurring states. If the value of  $\psi$  has been determined for constant weight, this second equation is given by  $\left(\frac{d\psi}{dx}\right)_{vT} = 0$ . If on the other hand we have determined the value of  $\psi$  for  $1-y$  simple and  $y$  complex molecules, this second relation must be found by putting the molecular thermodynamic potential for a complex molecule  $n$  times that of a simple molecule. But, as immediately follows from the equation given in These Proc. October 1902, p. 306, this may immediately be reduced to the preceding form, if in the second case the value of  $\psi$  is first divided by the weight of  $1-y$  simple molecules and  $y$  complex ones, so by  $1 + (n-1)y$ .

But whatever form we may choose for  $\psi$ , we get a second equation — and it follows from this that only a single curve lying on the  $\psi$ -surface indicates the really occurring states. This curve may be considered as the intersection of the  $\psi$ -surface with another surface

$\left(\frac{d\psi}{dx}\right) = 0$ ; and so we find the points of this curve by seeking the smallest value of  $\psi$  in every section of the  $\psi$ -surface for  $v =$  constant. Now too coexisting states will be given by points on the  $\psi$ -surface, for which the tangent planes coincide. If the double tangent plane is rolled when there is a spinodal and also a binodal line on the  $\psi$ -surface, only one single position will be of significance for really occurring states. The points of contact are then the points in which the curve under consideration intersects the binodal curve, the intersection with the spinodal curve giving the points between which unstable states are found. When the temperature has risen to above the critical temperature of the substance, and so when no coexisting states are possible any longer, the discussed curve must pass throughout its course, so between  $v = \infty$  and  $v = b$ , through points of the  $\psi$ -surface representing stable phases and so neither the spinodal nor the binodal line can extend over the whole breadth of the  $\psi$ -surface. At the critical temperature, the two points of intersection of the curve with the binodal, and also with the spinodal line coincide, and so the critical point is a plaitpoint on the  $\psi$ -surface.

The conditions for stability of a phase on the  $\psi$ -surface of a binary system are:

$$\left(\frac{d^2\psi}{dv^2}\right)_{xT} > 0$$

$$\left(\frac{d^2\psi}{dx^2}\right)_{vT} > 0$$

and

$$\left(\frac{d^2\psi}{dv^2}\right)_{xT} \left(\frac{d^2\psi}{dx^2}\right)_{vT} > \left(\frac{d^2\psi}{dx dv}\right)^2$$

or

$$-\left(\frac{dp}{dv}\right)_{xT} > 0$$

$$\left(\frac{d^2\psi}{dx^2}\right)_{vT} > 0$$

and

$$-\left(\frac{dp}{dv}\right)_{xT} - \frac{\left(\frac{dp}{dx}\right)_{vT}^2}{\left(\frac{d^2\psi}{dx^2}\right)_{vT}} > 0$$

The last form may be written:

$$-\left(\frac{dp}{dv}\right)_T > 0$$

and so can assume the simple form which holds for a simple substance, either with or without association. For

$$\frac{dp}{dv}_T = \left(\frac{dp}{dv}\right)_{xT} + \left(\frac{dp}{dx}\right)_{vT} \frac{dx}{dv}.$$

From  $\left(\frac{d\psi}{dx}\right)_{vT} = 0$  follows by differentiation

$$\left(\frac{d^2\psi}{dx dv}\right)_T dv + \left(\frac{d^2\psi}{dx^2}\right)_{vT} dx + \left(\frac{d^2\psi}{dx dT}\right)_v dT = 0$$

or

$$-\frac{dp}{dx}_{vT} dv + \left(\frac{d^2\psi}{dx^2}\right)_{vT} dx - \left(\frac{d\eta}{dx}\right)_{vT} dT = 0$$

or

$$-\left(\frac{dp}{dx}\right)_{vT} dv + \left(\frac{d^2\psi}{dx^2}\right)_{vT} dx - \left(\frac{d\varepsilon}{dv}\right)_{vT} \frac{dT}{T} = 0$$

So for constant value of  $T$  we have  $\frac{dx}{dv} = \frac{\left(\frac{dp}{dx}\right)_{vT}}{\left(\frac{d^2\psi}{dx^2}\right)_{vT}}$ ; if we substitute this value for  $\frac{dx}{dv}$  in the equation for  $\frac{dp}{dv}_T$ , the third condition of stability becomes:

$$-\frac{dp}{dv} > -\left(\frac{dp}{dv}\right)_{xT} - \frac{\left(\frac{dp}{dx}\right)_{vT}^2}{\left(\frac{d^2\psi}{dx^2}\right)_{vT}}$$

as we had derived from the theory of a binary system.

So the limits within which unstable states are found, lie further apart than would follow from  $\left(\frac{dp}{dv}\right)_{xT} = 0$ . They are determined by

$$-\left(\frac{dp}{dv}\right)_{xT} = \frac{\left(\frac{dp}{dx}\right)_{vT}^2}{\frac{d^2\psi}{dx^2}}$$

Only for the case that also  $\left(\frac{dp}{dx}\right)_{vT} = 0$ , they coincide with those of  $\left(\frac{dp}{dv}\right)_{xT} = 0$ .

In harmony with all this is also the circumstance that the critical point of the binary mixture for constant value of  $x$  still lies in the unstable region. In the critical point for a mixture with constant  $x$   $\left(\frac{dp}{dv}\right)_{xT} = 0$ , and so also  $\frac{dp}{da}$  positive. Accordingly the critical point of the substance in association is a plaitpoint, as we saw above. More similar remarks might be made, but all following from and in agreement with the consideration of an associating substance as a binary system.

### X. Shape of the $\psi$ -surface.

For the  $\psi$ -surface for constant weight we must assume for  $p$  the form :

$$p = \frac{RT \left(1-x + \frac{x}{n}\right)}{(v-b)_x} - \frac{a \left(1 - \frac{x}{2}\right)^2}{v_x^2}$$

if  $1-x$  represents the fraction of the weight that is present in the form of simple molecules, and  $x$  the fraction which occurs as complex molecules.

For the  $\psi$ -surface for constant number of molecules we must put :

$$p = \frac{RT}{(v-b)_y} - \frac{a \left[1 - y + \frac{n}{2}y\right]^2}{v_y^2}$$

if  $1-y$  represents the fraction which is present as simple molecules and  $y$  the fraction which occurs as complex molecules.

Between the quantities  $x$  and  $y$  exists the relation .

$$\frac{ny}{1-y} = \frac{x}{1-x}$$

For both the terms of this equation represent the ratio of the quantities by weight in the associated and unassociated form. Then we find :

$$\begin{aligned} x &= \frac{ny}{1-y+ny} \\ 1-x &= \frac{1-y}{1-y+ny} \\ 1-x + \frac{x}{n} &= \frac{1}{1-y+ny} \\ 1 - \frac{x}{2} &= \frac{1-y + \frac{n}{2}y}{1-y+ny} \end{aligned}$$

From the equality of  $p$ , whether this quantity is expressed in  $\bar{x}$  or in  $y$ , follows:

$$\frac{1 - x + \frac{x}{n}}{(v-b)x} = \frac{1}{(v-b)y} \text{ of } (v-b)_y = (1-y+ny)(v-b)_x,$$

and

$$\frac{\left(1 - \frac{x}{2}\right)^2}{v_x^2} = \frac{\left(1 - y + \frac{n}{2}\right)^2}{v_y^2} \text{ or } v_y = (1 - y + ny)v_x.$$

And so we find, what, indeed, might have been put at once:

$$b_y = b(1 - y + ny)$$

and so:

$$p = \frac{RT}{v_y - b_x(1 - y + ny)} \frac{a \left(1 - y + \frac{n}{2}\right)^2}{v_y^2}.$$

The quantity  $b_x$  is not dependent on  $x$ , and may be written without index. In the last form we can apply with the greatest certainty the criteria which have been found in the theory of a binary system to determine whether we have a mixture with decreasing or increasing value of  $T_k$  or perhaps with minimum value of  $T_k$ . The latter appears to be the case. The criterion for minimum  $T_k$  requires that a value of  $y$  can be determined between 0 and 1 which satisfies the relation:

$$\frac{1}{a_y} \frac{da_y}{dy} = \frac{1}{b_y} \frac{db_y}{dy}.$$

With  $a_y = a \left(1 - y + \frac{n}{2}y\right)^2$  and  $b_y = b(1 - y + ny)$  we find for the determination of  $y$  the equation:

$$\frac{n-2}{1 - y + \frac{n}{2}y} = \frac{n-1}{1 - y + ny}.$$

For  $y=0$  the first term viz.  $n-2$  is smaller than the second, which then becomes  $n-1$ . For  $y=1$  the first term is equal to  $2 \frac{n-2}{n}$ , and the second to  $\frac{n-1}{n}$ . So if  $2n-4 > n-1$  minimum  $T_k$  is present, so if  $n > 3$ . For the value of  $\frac{y}{1-y}$  we find  $\frac{2}{n(n-3)}$ , and so for  $\frac{x}{1-x}$  the value  $\frac{2}{n-3}$ .

From the form of  $p$  as function of  $x$  we might also have arrived at the same result by investigating whether the quantity:

$$-\frac{\left(1 - \frac{x}{2}\right)^2}{1 - x + \frac{x}{n}}$$

can assume a minimum value for values of  $x$  between 0 and 1. So we might determine  $x$  from:

$$-\frac{1}{1 - \frac{x}{2}} = -\frac{1 - \frac{1}{n}}{1 - x + \frac{x}{n}}$$

or

$$\frac{1}{1 - x + \frac{x}{2}} = \frac{n - 1}{n(1 - x) + x}$$

or

$$(n - 1)(1 - x) + \frac{x(n - 1)}{2} = n(1 - x) + x$$

or

$$\frac{x}{1 - x} = \frac{2}{n - 3}$$

or

$$x = \frac{2}{n - 1}$$

In harmony with this is the value

$$y = \frac{2}{(n - 1)(n - 2)}$$

Especially on the  $\psi$ -surface for constant number of molecules the mixture with minimum critical temperature lies very near the side of the component which has the smallest volume of the molecules. And it is to be expected that a mixture for which the plaitpoint line ( $p, T$ -projection) touches the  $p, T$ -projection of the critical points, does not exist. Such a point, viz. lies still more shifted towards the side of the component with the smallest  $b$ . Originally I gave the formula:

$$\frac{1}{a_y} \frac{da_y}{dy} = \frac{2}{3} \frac{1}{b_y} \frac{db_y}{dy} \quad (\text{Cont. II, p. 120})$$

for the determination of the concentration of such a mixture.

Later on (These Proc. March 1902, p. 548) I thought I had to conclude that the form:

$$\frac{1}{a_y} \frac{da_y}{dy} = \frac{f-2}{f-1} \frac{db_y}{b_y dy}$$

in which  $f = \left( \frac{T}{p} \frac{dp}{dT} \right)_{kr}$ , is more accurate.

Then we have for the determination of  $y$  the equation:

$$\frac{n-2}{1-y+\frac{n}{2}y} = \frac{f-2}{f-1} \frac{n-1}{1-y+ny}$$

The value of  $y$  satisfying this equation is:

$$y = \frac{f-n}{f} \frac{2}{(n-1)(n-2)}$$

If  $n > f$ , to which I have thought I had to conclude, then  $y$  is negative. In other words, then the point of contact of the plaitpoint line and the curve of the critical points does not occur. But this does also away with the principal reason why in the drawing of the two  $p, T$ -curves, viz. that of the plaitpoints and that of the critical points, for mixtures with minimum critical temperature, the distance of the two curves has been chosen so small.

The  $p, T$ -projection of the critical points begins at a temperature given by  $RT_{k_1} = \frac{s}{r(f-1)} \frac{a}{bg}$ , ends at  $RT_{k_2} = \frac{s}{r(f-1)} \frac{a n}{bg 4}$ , and has a minimum temperature given by  $RT_{km} = \frac{s}{r(f-1)} \frac{a n(n-2)}{bg(n-1)^2}$ . So whereas the final temperature is about or a little more than twice as high as the initial temperature, the temperature has first run back, and has fallen to the

$$\frac{n(n-2)}{(n-1)^2} = 1 - \frac{1}{(n-1)^2}$$

part of the initial temperature, so only a little lower than this, for  $x = \frac{2}{n-1}$  or  $y = \frac{2}{(n-1)(n-2)}$ . The value of  $p_k$  has continually

descended. In the initial point this value amounts to  $\frac{a}{bg^2 r^2 (f-1)}$ ,

at the minimum temperature it amounts to the  $\left( \frac{n-2}{n-1} \right)^2$  part of

$\frac{a}{bg^2} \left( \frac{n-2}{n-1} \right)^2$ , so to somewhat more than  $\frac{2}{3}$  of the original amount —

and the final value is the  $\frac{1}{4}$  part of the initial value. The temperature for the curve of the plaitpoints of course coincides with that of the critical points for  $T_{k_1}$  and for  $T_{k_2}$ , but is higher for all intermediate values of  $x$  or  $y$ . Only if there should be a mixture for which the two curves are in contact, they will of course again coincide. If this point of contact exists, which if we start from the initial point, lies before the point where minimum temperature exists, it follows from this that also the plaitpoint curve must begin with retrograding to lower temperatures. But this cogent reason for the retrogression of the plaitpoint line is wanting here. And so the question may be raised, if when this point of contact is absent, the plaitpoint line may perhaps begin with running to higher temperatures. For the particular  $\psi$ -surface of an associating substance the answer to this question is of no or rather of very little importance. But for the theory of the binary systems in general it is of greater importance. If the question should have to be answered in the affirmative, the  $T,x$ -projection of the plaitpoint line need not present a minimum for  $T_{pl}$ , and the existence of double retrograde condensation, which I discussed (These Proc. March 1909) would not be necessary. Then we meet, however, with other difficulties, which I cannot discuss here.

For the  $\psi$ -surface of an associating substance the matter would be settled if it was possible to prove that the value of  $T_k$  for the substance when there is no association is just as high as or lower than the value of  $T_{pl}$  in the case of association.

If we seek  $T_k$  for the case when :

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

we find for the determination of  $T_k$  :

$$\frac{RT_k}{(v-b)^2} \left( 1 - \frac{db}{dv} \right) = \frac{2a}{v^3}$$

and for the determination of  $v$  :

$$\frac{2}{(v-b)} \left( 1 - \frac{db}{dv} \right) + \frac{\frac{d^2b}{dv^2}}{1 - \frac{db}{dv}} = \frac{3}{v}$$

or

$$\frac{2v}{v-b} \left( 1 - \frac{db}{dv} \right) + \frac{v}{2} \frac{\frac{d^2b}{dv^2}}{\left( 1 - \frac{db}{dv} \right)} = \frac{3}{2}$$

But even though we restrict ourselves to the simplified form:

$$\frac{b}{bg} = 1 - \alpha \frac{bg}{v}$$

the determination of  $v$  requires the knowledge of  $\alpha$ , and also the determination of  $v$  becomes uncertain and so also the determination of:

$$RT_k = \frac{2a(v-b)^2}{v^3} \frac{1}{1 - \frac{db}{dv}}$$

It appears that  $RT_k$  differs very little from  $\frac{a}{bg} \frac{1}{r(f-1)}$  (p.118 These Proc. June 1910). But whether this difference is positive or negative is not to be stated with certainty.

For the present I shall have to leave this an open point.

In the equation

$$MRT v^3 - 2a(v-b)^2 = \frac{y(1-y)}{2} a_y \left( \frac{v}{a_y} \frac{da_y}{dy} - 2 \frac{db_y}{dy} \right)^2$$

(of § 21 Cont. II) there is, indeed, a means to be found to get information about the different circumstances in the course of the spinodal line in the immediate neighbourhood of the axes  $x=0$  and  $x=1$ , at least qualitatively, for mixtures for which the minimum value of  $T_k$  lies at very small value of  $y$ . The above simple equation namely holds, if  $a_1 a_2 = a_1^2$ , which will be the case for quasi-association.

Let us put the value of  $T$  equal to  $T_k$  for  $y=0$ , and so  $MRT v_1^3 = 2a_1(v_1-b_1)^2$ , and further, what has always been assumed in the derivation of this equation  $\frac{db_y}{dv} = 0$  and  $MRT_k = \frac{8}{27} \frac{a_1}{b_1}$  and  $v_1 = 3b_1$ .

Let us now seek how many points of intersection a line  $v=v_1$  possesses with the spinodal line. As  $a_y = a_1 \left( 1 + \frac{n-2}{2} y \right)$  and  $b_y = b_1 [1 + (n-1)y]$ , the above equation becomes.

$$\begin{aligned} MRT_k 27b_1^3 - 2a_1 \left( 1 + \frac{n-2}{2} y \right)^2 [3b_1 - b_1 - b_1(n-1)y]^2 = \\ = \frac{y(1-y)}{2} a_1 \left( 1 + \frac{n-2}{2} y \right)^2 \left\{ \frac{3b_1(n-2)}{1 + \frac{n-2}{2} y} - 2(n-1)b_1 \right\}^2 \end{aligned}$$

or if we divide by  $8 a_1 b_1^2$ :

$$1 - \left(1 + \frac{n-2}{2}y\right)^2 \left(1 - \frac{n-1}{2}y\right)^2 = \frac{y(1-y)}{16} \left\{3(n-2) - 2(n-1) - (n-1)(n-2)y\right\}^2$$

If for  $x=0$  or  $x=1$  we had just minimum critical temperature, then :

$$\left(\frac{1}{a_y} \frac{da_y}{dy}\right)_1 = \left(\frac{1}{b_y} \frac{db_y}{dy}\right)_1$$

would be, or  $n-2 = n-1$ , which might only be put for  $n = \infty$ ; if the above mentioned point of contact of plaitpoint line and critical line was just there, then would be :

$$\left(\frac{1}{a_y} \frac{da_y}{dy}\right)_1 = \frac{2}{3} \left(\frac{1}{b_y} \frac{db_y}{db}\right)_1$$

or

$$3(n-2) = 2(n-1)$$

which would hold for  $n=4$ . Assuming intermediate properties for the initial point, we must put :

$$\left(\frac{1}{a_y} \frac{da_y}{dy}\right)_1 = k \left(\frac{1}{b_y} \frac{db_y}{dy}\right)_1$$

in which  $k$  lies between 1 and  $\frac{2}{3}$ . That I put here  $\frac{2}{3}$ , and not as

above  $\frac{f-2}{f-1}$  is in accordance with what I have said about the simplifications which have been applied in the derivation of the discussed equation.

So we have here :

$$(n-2) = k(n-1)$$

So  $k$  approaches unity in connection with the high value of  $n$ , and the minimum critical temperature lies only a very little distance from the axis  $x=0$ .

Now we have to examine the value of  $y$  in the equation :

$$1 - \left(1 - \frac{n-2}{2}y\right)^2 \left(1 - \frac{n-1}{2}y\right)^2 = \frac{y(1-y)}{16} \{n-4 - (n-1)(n-2)y\}^2$$

For  $y=0$  this equation is satisfied, and so the critical point for  $x=0$  is a point of the spinodal curve. It is self-evident that the line  $v=v_1$  can only present points of intersection with the branch of the spinodal line which lies on the liquid side. If we divide both the members of the equation by  $y$ , we get a third-power equation apparently, which, however, simplifies to a 2<sup>nd</sup> power equation, because

the quantity  $-\frac{(n-1)^2(n-2)^2}{16}y^3$  occurs in both members, which quantity accordingly is cancelled. This quadratic equation can either have two positive roots, or one positive root and a negative one, which depends on the value of  $n$ .

But without ascertaining the significance of the different points of intersection in connection with the number of the roots of the equation we immediately find *for small values of  $y$*  an answer to the question which has been put here, if we replace the equality of the two members of the equation by, what is the criterion of stability,

$$1 - \left(1 - \frac{n-2}{2}y\right)^2 \left(1 - \frac{n-1}{2}y\right)^2 > \frac{y(1-y)}{-16} \{(n-4) - (n-1)(n-2)y\}^2$$

or for small value of  $y$  by :

$$y > \left(\frac{n-4}{4}\right)^2 y$$

So when  $\left(\frac{n-4}{4}\right)^2 > 1$ , the spinodal curve extends over the whole breadth, and the temperature must rise above  $T_k$  from the very beginning.

We might make this result more comprehensible by observing that for a mixture with minimum critical temperature splitting up of the line  $\frac{d^2\psi}{dv^2} = 0$  takes place at  $(T_k)_{min}$ ; but that splitting up of the spinodal line does not take place until higher temperature, and then at another value of  $y$ , too. So the double point shifts, and according to our result, to the side from which  $(T_k)_{min}$  is not far distant. For  $\left(\frac{n-4}{4}\right)^2 = 1$  the double point reaches the edge. For smaller value of  $n$  it does not reach the edge yet. On account of the approximative character of the equation under discussion all this can of course, not be considered as a conclusive proof, and the result will not be numerically accurate. But the result is in such close agreement with what we could expect a priori, viz. that it must be possible that the plaitpoint line rises at first even for mixtures with  $(T_k)_{min}$ , that I think that we may safely assume this possibility. But all this can only occur if the value of  $y$ , for which  $T_k$  has minimum value, is very small. If  $y$  for  $(T_k)_{min} = 0$ , this would be self-evident.