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Physics. — Prof. J. D. van der Waals on: "*Ternary Systems*." II. (Continued from page 463).

It occurs frequently in a binary mixture that two phases coexist which have the same concentration. In this case the pressure when we move along the connodal curve is either maximum or minimum. An isobar may then be drawn, touching both the liquid- and the vapour branch, and the isobars of other values of p cut then both branches twice. The ζ-curves for such a binary mixture will have a much more complicated shape than I have given up to now, and if we should now have a ternary system in which one or two or the three pairs which may be formed from it show this particularity then the ζ-surface will also show particularities whose main features we shall examine. As a *minimum* pressure has not yet been observed for normal substances, we shall only discuss the case of *maximum* pressure.

The property that for a binary system the concentration of liquid and vapour are the same, coheres with another property for such systems, which I have discussed, Cont. II, p. 86, though I have neglected to point out the relation between these two properties. This second property and the relation is found from the following formula. One of the conditions for coexistence is:

$$\left(\frac{\partial \psi}{\partial x_1}\right)_{v_1 T} = \left(\frac{\partial \psi}{\partial x_2}\right)_{v_2 T}.$$

We write

$$\psi = f(x) - \int p\, dv,$$

and so

$$\left(\frac{\partial \psi}{\partial x}\right)_{vT} = f'(x) - \int \left(\frac{\partial p}{\partial x}\right)_{vT} dv.$$

For the case that $x_1 = x_2$ we derive from the above formulae:

$$\int_{v_2}^{v_1} \left(\frac{\partial p}{\partial x}\right)_{vT} dv = 0$$

which equation occurs already in Théor. Mol. Arch. Néerl. XXIV.

In order that $\left(\frac{\partial p}{\partial x}\right)_{vT} dv$, integrated between the liquid and the vapour volume, be equal to 0, $\left(\frac{\partial p}{\partial x}\right)_{vT}$ must be equal to zero somewhere between these two volumes. In consequence the particularity that mixtures may be formed, for which $x_1 = x_2$ occurs only when a locus exists in the xv diagram, along which $\left(\frac{\partial p}{\partial x}\right)_{vT} = 0$. Accordingly QUINT has observed the circumstance that, keeping T constant the curve $p = f(x, v)$ in the mixture of HCl and C_2H_6 shows a maximum. In Cont. II p. 86. I have discussed such a locus, and proved that for great volumes it has an asymptote parallel to the volume-axis, and that for small volumes it moves to the side of the component for which b is greater. In fig. 7 the dotted line passing through P and Q, represents this locus. On the left of this curve $\left(\frac{\partial p}{\partial x}\right)_{vT}$ is positive, and on the right negative. All the isobars must then possess a tangent parallel to the x-axis in the points where they cut this locus. In fig. 7 the course of some curves of equal pressure has been traced. The temperature is assumed to be so low that the plait on the ψ-surface stretches over the whole breadth of the diagram, and so the curve, for which $\left(\frac{\partial p}{\partial v}\right)_{xT} = 0$, continues to consist of two isolated branches. The curves $L\,P\,M$ and $L'\,Q\,M'$ represent these branches, viz. the dotted ones.

The limits of the unstable region are somewhat wider, and they are also indicated as passing through L, P and M, or L', Q and M'; in the figure they are indicated by lines of alternately larger and smaller dots. That these limits of the unstable region must pass through P and Q, follows from the property, that if $\left(\frac{\partial p}{\partial x}\right)_{vT}$ is equal to 0, the condition:

$$\frac{\partial^2 \psi}{\partial x^2}\frac{\partial^2 \psi}{\partial v^2} - \left(\frac{\partial^2 \psi}{\partial x\,\partial v}\right)^2 = 0$$

is satisfied in the points, in which $\frac{\partial^2 \psi}{\partial v^2} = -\left(\frac{\partial p}{\partial v}\right)_x = 0$ is.

If we closely examine the character of the points P and Q, we conclude that p in the point Q is really a maximum. The point Q,
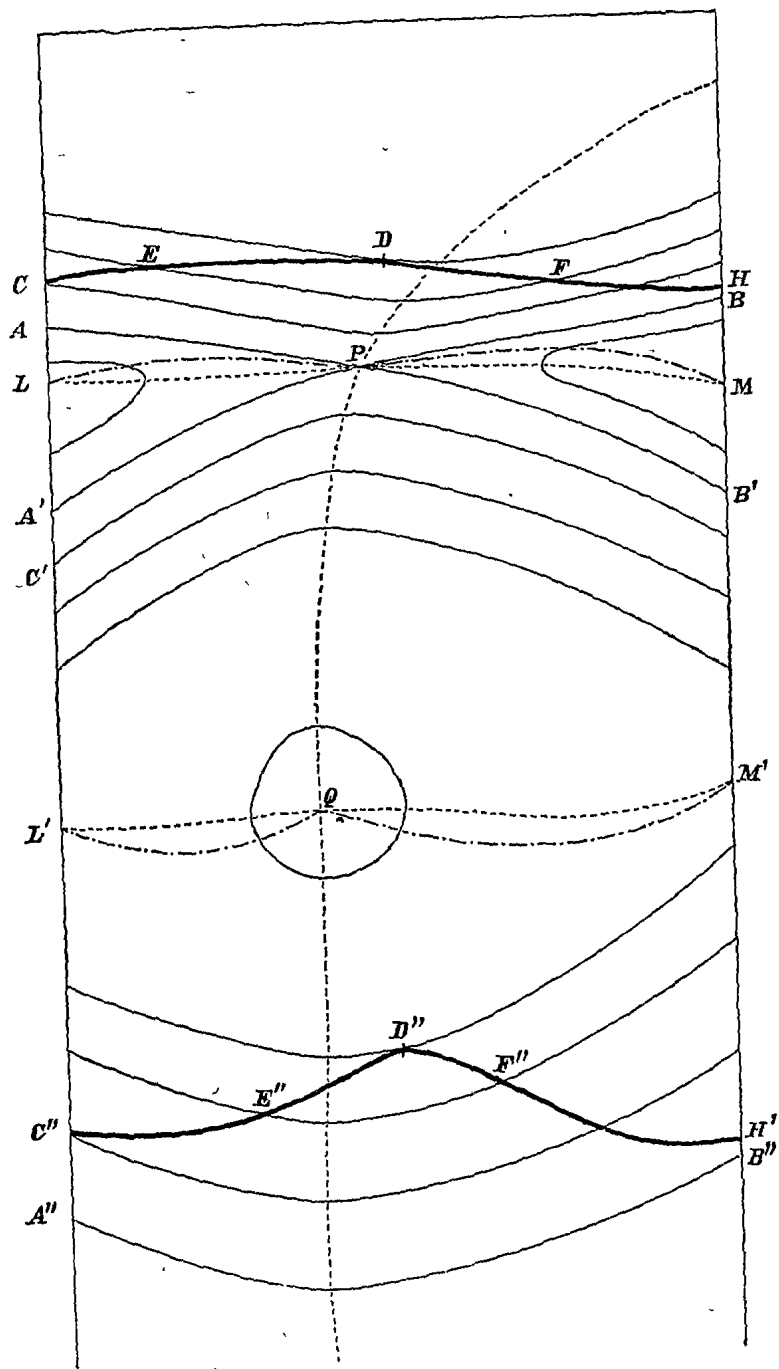
Fig. 7.

namely, lies on the isothermal of the concentration x_Q and on that isothermal it is the point where the pressure is maximum while on

36

a section parallel to the x-axis, the value of p is also maximum. The point P on the other hand, lying on the isothermal of the concentration x_P, represents a phasis for which the pressure on the isothermal is minimum, while p along a line parallel to the x-axis in P, is maximum. From this follows 1st. that the isobar passing through P has a double point in the point P, and 2nd that the lines of equal pressure enclose the point Q, — and in such a way that as the pressure approaches that of Q, the closed curves get narrower, and keep also entirely within the limits of $x = 0$ and $x = 1$ and are completely enclosed in the xv diagram.

The isobar through P had a shape which may be considered as transition form between the shapes for pressures which are greater, and pressures which are smaller than p_P. For pressures which are greater the isobar consists of two separate branches, viz. 1st. a closed curve round Q and 2nd a branch lying above P and which therefore, remaining on the liquid sheet, belongs to a volume smaller than that of P. In fig. 7 we can take for it e. g. the branch passing through C, which must show a maximum-volume on the dotted line. Then the closed curve of Q, belonging to the same isobar, is indicated by the curves passing through C' and C''. For the isobar of P these two separate branches have drawn so near each other, that they have met in P. Accordingly this isobar has the following shape, indicated by $APB'B''A''A'PB$. The points B' and B'' must be thought connected by a piece lying outside $x = 1$ and in the same way the points A'' and A' by a piece outside $x = 0$. The lines of equal pressure for $p < p_P$ must fill up the space lying within APA' and BPB' and that below $A''B''$. A similar curve, provided $p > p_L$, begins below A on the curve $x = 0$, passes on to greater values of x, has a tangent parallel to the v-axis on the locus for which $\left(\dfrac{\partial p}{\partial v}\right)_x = 0$, and then returns to smaller values of x. It is continued for vapour volumes greater than that of $A''B''$, and appears again between BPB' provided p be also greater than P_M. The shape between BPB' is analogous to that of APA'.

In order to find the mixture for which liquid and vapour concentration is equal, we must determine on a line, parallel to the v-axis two points chosen on the same isobar, in such a way that $\displaystyle\int_{v_2}^{v_1}\left(\dfrac{\partial p}{\partial x}\right) dv = 0$. In the figure the points D' and D'' have been

chosen for this. Of course one point D had to be taken on the left of the locus PQ, the other on the right.

The pressure on the connodal curve being maximum for that mixture, the connodal curve must touch a curve of equal pressure both in D and in D'. On the left and on the right of D and also of D' the connodal curve must pass on to isobars of lower pressure. If we assume the maximum pressure of the first component at the chosen temperature to be equal to p_C, and that of the second component to be lower e.g. p_B, the connodal curve has a shape as is represented by the somewhat heavier curves $CEDFB$ and $C''E''D''F''B''$. But we must take care that $x_{E'} > x_E$ and $x_{F''} < x_F$.
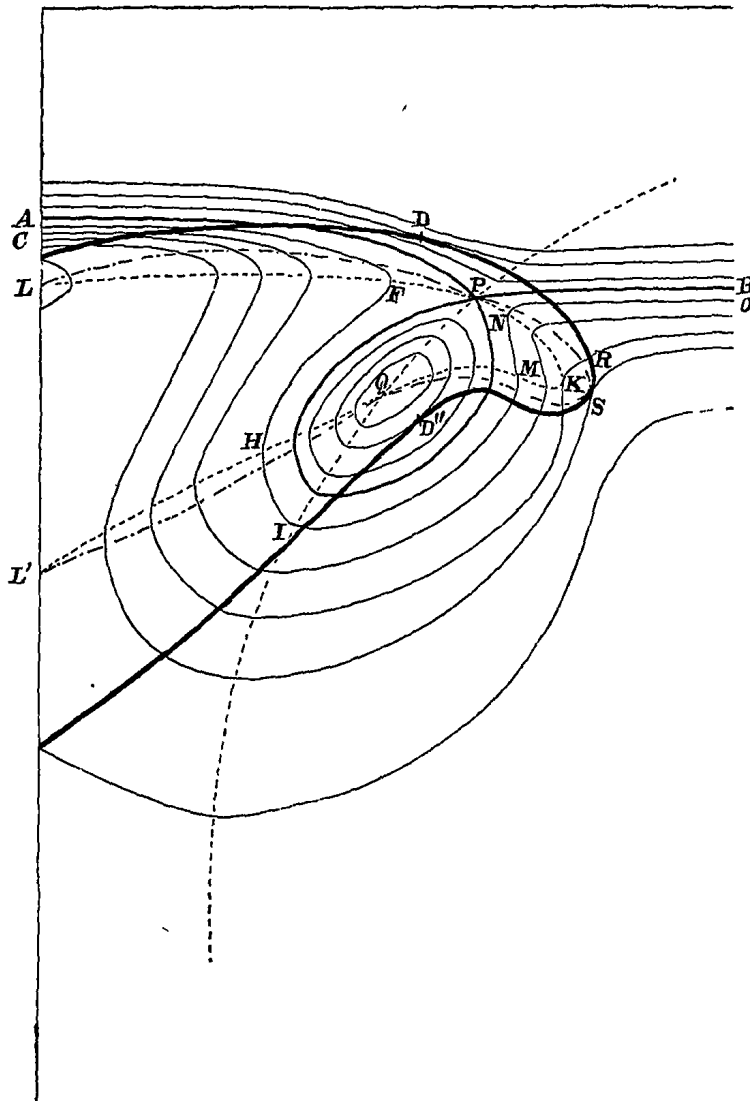

Fig. 8.

36*

The accurate knowledge of the course of the isobars is required
for indicating the value of ζ at every value of p for the binary
mixture and so also for the description of the shape of the ζ-surface
for a ternary mixture, if the here discussed peculiarity occurs for
at least one of the pairs. And in order to be able to do this also
at higher temperatures, at which the critical phenomena occur, and
because the course of the isobars at such temperatures is greatly
modified, 1 have represented this modification in Fig. 8 (pag. 543).

The principal modification, which is to be introduced in fig. 7,
and which leads to fig. 8 is this, that the isobar through P presents
its whole closed curve within the limits of $x = 0$ and $x = 1$. The
curve PQ has slightly changed its place and its shape (see Cont.
II pag. 88), but the change is comparatively small. That the whole
curve keeps within the xv-diagram follows from two circumstances.
1st . The pressure of P, which is a minimum pressure on the iso-
thermal of x_P, lies but little below that which can be realised as
liquid phasis, if the temperature is close to that at which both
minimum- and maximum pressure disappear and 2nd the difference
of pressure along a connodal curve generally increases at higher
temperatures. The whole curve showing itself, the course of isobars
for which $p < p_P$ can also take place without interruption within
the whole xv-diagram — at least for values of p lying above a
certain limit which may be derived from the preceding conside-
rations without nearer indication. If we follow such an isobar, e.g.
$CFHIMNO$, it must be possible to draw a tangent parallel to the
v-axis in F and H and also in M and N, in which four points the

curve for which $\left(\frac{\partial p}{\partial v}\right)_x = 0$ is cut; in point I, in which the curve for

which $\left(\frac{\partial p}{\partial x}\right)_v = 0$, is cut, the tangent must be parallel to the x-axis

Between F and H, and also between M and N the value of x
retrogrades. For the isobar passing through K the retrogression on
the left side of the figure continues, but it has just ceased on the
right side.

In fig. 8 point S indicates the plaitpoint and the isobar passing
through S must therefore touch the connodal curve in that point.
In the same way the connodal curve must touch a curve of equal
pressure in the points D and D'. All this proves that the tempe-
rature is thought to be so high, that there is still question of a
maximum pressure on the connodal curve. (Consult the observations
of KUENEN and those of QUINT for mixtures which have minimum-
critical temperature). Between S and R is retrograde condensation

*of the second kind and the fact that the values of x_R and x_S differ
so little is in accordance with the fact that it is very difficult to
prove r. c. II experimentally.*

Let us now proceed to describe the shape of ζ for the binary
mixture, in the first place according to fig. 7, so at lower tempe-
ratures. Let us begin with $p < p_L$, so p smaller than the mini-
mum pressure of the isothermal of the first component. We assume
this value of p_L to be greater than 0. In this case has ζ one
value, at least on the side of $x = 0$. As soon as p is chosen some-
what greater than p_L, there are three values of the volume for
small values of x and so also for ζ. If we apply the same consi-
derations to values of x near $x = 1$, p_M must be substituted for
p_L. The whole curve consists then, for p somewhat larger than
p_L and p_M, first of a continuous curve (vapour branch), and further
of two separate parts lying on the right and the left, each termi-
nating in a cusp (see fig. 9).

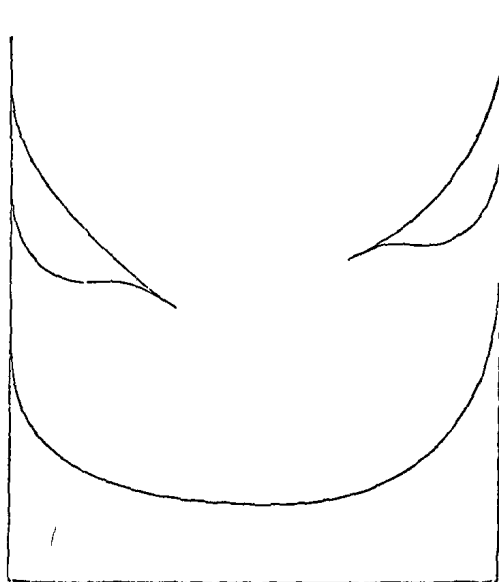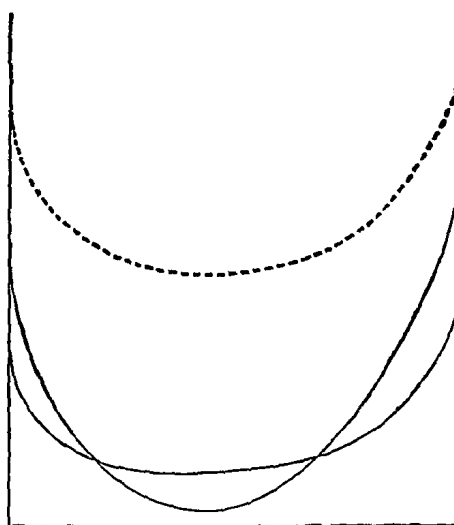Fig 9.   Fig 10

If p has increased to the value which the pressure has on the
line with the loop, the two cusps in fig. 9 have met, and the
upper branches on the right have coincided with those on the left
and form two curves with a double point. This is the case which
I mentioned in note (1) on p. 459. In this case the vapour branch
lies still lowest, then follows the liquid branch which shows a
discontinuity, and above it again the branch of unstable conditions,
also showing a discontinuity.

As soon as the pressure has increased to p_C (the maximum tension of the first component) the vapour branch has moved so far upward that it has reached the liquid branch on the left side of the figure. For the right side this would take place for $p = p_H$ (maximum tension of the second component). And for pressures between p_C and p_D the gas- and liquid branches have a double point on the left of x_D — in the same way for pressures between p_H and p_D a double point on the right of x .

For pressures above P_D the gas-branch has moved above the liquid branch; for $p = P_D$ these two branches touched each other. If the pressure is made to draw near to p_Q, the gas-branch and the branch of unstable phases form a closed curve, which has a cusp right and left, which curve is reduced to a point for $p = p_Q$, and for still higher values of p also this point has disappeared, and only the liquid branch remains.

We shall be brief in the discussion of the value of ζ at different pressure at the temperature assumed in fig. 8. The ζ-curve for the pressure $p = p_C$ is represented in fig. 11; the four cusps lie at x_F, x_H, x_M and x_N. For a somewhat lower pressure $p = p_K$ the right crest has disappeared, and for a still lower pressure $p = p_S$ (plaitpoint pressure) the right part of ζ is curved continuously. So we have here between S and R retrograde condensation of the second kind. I shall leave the modification of ζ for pressures greater than p_C undiscussed.
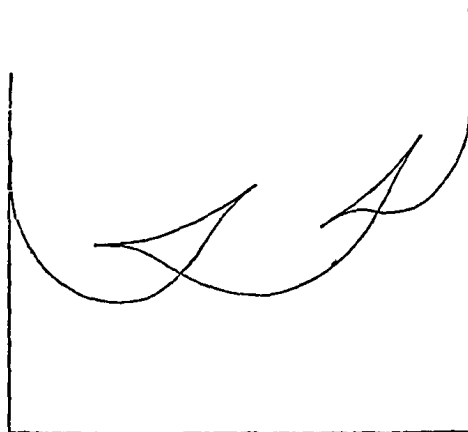

Fig. 11.

For a binary mixture I have pointed out that there is a connection between the circumstance that two phases of equal concentration can coexist, and the circumstance that for a mixture of the two components of that system a minimum critical temperature

occurs. The existence of such a connection having since been perfectly confirmed by the experiments of KUENEN and QUINT, we are naturally led to investigate whether a minimum-critical temperature can occur also for a mixture of three substances — and what are the conditions for the existence of such a minimum critical temperature. That connection could however not follow and could not be derived simply from the principle of continuity, but considerations of a molecular-theoretical nature were required to conclude to the existence of such a connection. Therefore I shall at the moment, as we consider it only our task to examine what follows for a ternary system from the assumption of continuity, refrain from seeking the conditions which the components must satisfy in order to be able to form a mixture which possesses maximum pressure and assume only that a mixture can really be formed from the three chosen components for which' liquid and vapour are composed in the same way and whose coexistence pressure is therefore maximum.

If we take the pressure somewhat smaller than that maximum pressure, so that we get a section of vapour and liquid sheet as drawn in fig. 10 for every section normal to the xy-surface passing through the point representing that special mixture, the connodal curve will consist of two closed curves, of which the inner curve indicates the vapour phasis. If p is equal to that maximum pressure, the two closed curves have been reduced to one point, the point where the two sheets touch each other. Under a still greater pressure the vapour sheet will have risen quite above the liquid sheet. With decreasing pressure the two closed curves extend, and if we took only the principle of continuity into account, a great many cases would be possible. For instance the extending closed curves might reach the sides of the triangle which represent the pairs of which the ternary system consists, and cut them in two points, either one side or two sides, or all three the sides. In the last case the three pairs which compose the ternary system, would possess all three the properties of maximum pressure. But an extension is also possible, at which the second and the third side is never cut twice — and even one at which none of the sides is cut twice, and at which therefore the closed curve which extends and which is changing its shape, reaches the sides of the triangle for the first time in one of the angles. In this case the ternary system would have maximum pressure, without this being the case with any of the pairs of which it consists. The investigation of conditions which are required for a minimum critical temperature will probably be able to decide the

question as to the possibility of these cases. But I shall not enter into this subject at least for the present.

Between the two closed parts of which the projection of the connodal curve on the xy-surface consists, lies another closed curve, the projection of the double points. The curve, which consisted of one branch in the case discussed on page 460 within the triangle OAB, consists in this case of two branches lying within the triangle. At any rate it will always consist of two branches theoretically; but for the ζ-surface we need only to know that part which lies within the triangle. When p has the value of the before-mentioned maximum pressure, the closed curve of double points too contracts to one point. This point is the same as that to which the two closed parts of the connodal curve contract.

If for a moment we take recourse to molecular-theoretical considerations to derive properties of the locus of the double points, we should write down the equation of p. 461 in this way:

$$log \frac{p_{cr}}{p} = f\left(\frac{T_{cr}}{T} - 1\right).$$

In this equation which holds good at least as an approximation, we put $f =$ constant and $p_{cr} = \frac{1}{27}\frac{a}{b^2}$ and $\frac{T_{cr}}{273} = \frac{8}{27}\frac{a}{b}$.

Keeping T constant, we get by differentiation:

$$\frac{dp}{p} = \left(\frac{da}{a} - 2\cdot\frac{db}{b}\right) - f\frac{T_{cr}}{T}\left(\frac{da}{a} - \frac{db}{b}\right)$$

or

$$\frac{dp}{p} = \left(f\frac{T_{cr}}{T} - 2\right)\frac{db}{b} - \left(f\frac{T_{cr}}{T} - 1\right)\frac{da}{a}.$$

Keeping p constant we find the condition:

$$\frac{\frac{da}{a}}{\frac{db}{b}} = \frac{f\frac{T_{cr}}{T} - 2}{f\frac{T_{cr}}{T} - 1}.$$

In the limiting case, for continually decreasing values of T, the value of the second member $= 1$, and so:

$$\frac{1}{a}\left(\frac{\partial a}{\partial x} + \frac{dy}{dx}\frac{\partial a}{\partial y}\right) = \frac{1}{b}\left(\frac{\partial b}{\partial x} + \frac{dy}{dx}\frac{\partial b}{\partial y}\right),$$

from which for the projection of the curve of the pressures of coincidence at very low temperatures follows:

$$\frac{dy}{dx} = -\frac{\dfrac{1}{a}\dfrac{\partial a}{\partial x} - \dfrac{1}{b}\dfrac{\partial b}{\partial x}}{\dfrac{1}{a}\dfrac{\partial a}{\partial y} - \dfrac{1}{b}\dfrac{\partial b}{\partial y}}$$

or

$$\frac{dy}{dx} = -\frac{\dfrac{\partial \dfrac{a}{b}}{\partial x}}{\dfrac{\partial \dfrac{a}{b}}{\partial y}}.$$

If $\dfrac{dy}{dx}$ has an arbitrary value, as is the case when the locus has

been reduced to a point, then $\dfrac{\partial \dfrac{a}{b}}{\partial x}=0$, and in the same way $\dfrac{\partial \dfrac{a}{b}}{\partial y}=0$,

i. e. $\dfrac{a}{b}$ and so also T_{cr} must be capable of having a minimum. In this way we arrive therefore for a ternary system at the same result, as I had formerly obtained for a binary system, also for the limiting case of low temperatures.

If we do not consider the limiting case, which would correspond with $T=0$, but if we give T a definite value, we find:

$$d\frac{a}{b} = -\frac{1}{f\dfrac{T_{cr}}{T}-1}\frac{a}{b}\frac{db}{b},$$

from which follows that for the maximum pressure at temperature $= T$ the values of x and y are found from the two following equations

$$\frac{\partial \dfrac{a}{b}}{\partial x} = -\frac{1}{f\dfrac{T_{cr}}{T}-1}\frac{a}{b}\frac{1}{b}\frac{\partial b}{\partial x}$$

and

$$\frac{\partial \frac{a}{b}}{\partial y} = - \frac{1}{f \frac{T_{cr}}{T} - 1} \frac{a}{b} \frac{1}{b} \frac{\partial b}{\partial y}.$$

If we assume that b decreases with x, $\frac{a}{b}$ must increase with x and in the case of a minimum it must have passed that minimum. So the point for which the coincidence pressure is maximum, and for which also there is equality of composition of liquid- and vapour phasis, lies more to the side of the components with the smallest molecules than the point indicating the mixture with minimum-critical-temperature — and this will be the more so in proportion as T is higher.

For the case that T_{cr} as function of x and y might be represented by approximation as a plane (see Cont. II, p. 153) we find $\frac{dy}{dx} =$ constant, and so the line of the double points under a constant pressure is a straight one.

RELATION OF VOLUME, CONCENTRATION AND TEMPERATURE FOR COEXISTING PHASES OF A TERNARY SYSTEM.

In fig. 2 of the preceding communication the curve $ABPRB'A$ represents the projection of the connodal curve on the ψ-surface of a binary system in the xv-diagram at a constant temperature. This line may also be taken as representing the relation between molecular volume and concentration of a binary mixture at given temperature. If the temperature was put lower, this curve would have consisted of two isolated branches, one representing the liquid volumes, and the other the gas-volumes. Let us now think as third axis, a y-axis, and let us think also in the oyr-plane a similar curve drawn for a binary mixture that consists of the first and the third substance. If we further draw for every point of the right-angled triangle of the oxy-plane the volume at which a mixture represented by that point loses or resumes its homogeneity at increasing pressure, we get a surface which consists of two isolated sheets at low temperatures, and which at higher temperatures e. g. when T is above T_{cr} of one of the components, is contracted to one sheet.

If T is increased the form of the surface is modified in that sense that the new surface lies quite within that of lower temperature. At least for substances which do not enter into chemical combinations with each other, and which continue to consist in them-

selves of invariable molecules — so which do not associate to more complicate atom-groups.

For a binary mixture I have (Cont. II p. 101) derived the differential-equation for the relation between v, x and T. We shall be able to find in the same way the differential equation for the relation between v, x, y and T.

For coexistence of two phases of a ternary system, distinguishing the phases by the indices 1 and 2, the following equations must be satisfied

$$\left(\frac{\partial \psi}{\partial v}\right)_1 = \left(\frac{\partial \psi}{\partial v}\right)_2$$

$$\left(\frac{\partial \psi}{\partial x}\right)_1 = \left(\frac{\partial \psi}{\partial x}\right)_2$$

$$\left(\frac{\partial \psi}{\partial y}\right)_1 = \left(\frac{\partial \psi}{\partial y}\right)_2$$

and

$$\psi_1 - v_1 \left(\frac{\partial \psi}{\partial v}\right)_1 - x_1 \left(\frac{\partial \psi}{\partial x}\right)_1 - y_1 \left(\frac{\partial \psi}{\partial y}\right)_1 =$$

$$= \psi_2 - v_2 \left(\frac{\partial \psi}{\partial v}\right)_2 - x_2 \left(\frac{\partial \psi}{\partial x}\right)_2 - y_2 \left(\frac{\partial \psi}{\partial y}\right)_2$$

in which $\frac{\partial \psi}{\partial v}$ represents $\left(\frac{\partial \psi}{\partial v}\right)_{xyT}$ etc.

If the concentration for the first phasis is given, and so x_1 and y_1, then the quantities v_1, x_2, y_2 and v_2 are determined by the four above equations, and so the properties of the coexisting phasis. But in order to calculate them all the equations would have to be known, for which the knowledge of the equation of state is required. Even if we make use of them, the intricacy of these forms does not admit of the solution of the unknown quantities. Results, however, can be derived from the differential equation, even if we do not know these quantities accurately, and these results are not without interest. In the same way as is followed in Cont. I page 102 for a binary mixture, we find for a ternary system :

- 14 -

$$(v_2-v_1)\left\{\frac{\partial^2\psi}{\partial v_1{}^2}dv_1 + \frac{\partial^2\psi}{\partial v_1\partial x_1}dx_1 + \frac{\partial^2\psi}{\partial v_1\partial y_1}dy_1\right\} +$$

$$+ (x_2-x_1)\left\{\frac{\partial^2\psi}{\partial v_1\partial x_1}dv_1 + \frac{\partial^2\psi}{\partial x_1{}^2}dx_1 + \frac{\partial^2\psi}{\partial y_1\partial x_1}dy_1\right\} +$$

$$+ (y_2-y_1)\left\{\frac{\partial^2\psi}{\partial v_1\partial y_1}dv_1 + \frac{\partial^2\psi}{\partial x_1\partial y_1}dx_1 + \frac{\partial^2\psi}{\partial y_1{}^2}\right\} + (\varepsilon_{21})_v\frac{dT}{T} = 0 \ \ldots \ldots (1)$$

The quantity $(\varepsilon_{21})_v$ is, see l.c. p. 104, for normal substances a negative quantity.

If we keep T constant for the moment, so if we inquire into properties of one of the before-mentioned surfaces, we can derive the following rule for the position of the line that connects the two coexisting phases. If we for instance imagine on the liquid sheet a point determined by v_1, x_1 and y_1 and if we inquire into the direction of the line connecting the coexisting phasis with the chosen liquid phasis, so into the quantities proportionate to v_2-v_1, x_2-x_1 and y_2-y_1, we bring in point 1 as center a quadric surface:

$$\frac{\partial^2\psi}{\partial v_1{}^2}v^2 + \frac{\partial^2\psi}{\partial x_1{}^2}x^2 + \frac{\partial^2\psi}{\partial y_1{}^2}y^2 + 2\frac{\partial^2\psi}{\partial x_1\partial v_1}xv + 2\frac{\partial^2\psi}{\partial y_1\partial v_1}yv + 2\frac{\partial^2\psi}{\partial x_1\partial y_1}xy = C. \quad (2)$$

We cut that surface through the tangent plane at the liquid sheet, then the direction of the line connecting the two nodes, will be conjugate to the section of tangent plane and quadric surface cosines. The locus of the middle of the chords, whose cosines are equal to λ, μ and ν, is given by:

$$\lambda\frac{\partial f}{\partial v} + \mu\frac{\partial f}{\partial x} + \nu\frac{\partial f}{\partial y} = 0$$

and this equation leads to (1), when in equation (1) dT is put equal to 0 and when dv, dx and dy, are substituted for v, x and y and so when this middle plane is tangent plane to the v, x, y-surface under consideration.

On account of the importance which the surface represented by (2) has for the equilibrium of the ternary systems, it deserves a closer examination.

If a definite quantity of a substance, which is ternary composed, is to be in equilibrium at given temperature in a given volume then $\frac{\partial\psi}{\partial v}$, $\frac{\partial\psi}{\partial x}$, $\frac{\partial\psi}{\partial y}$ and $\psi - v\frac{\partial\psi}{\partial v} - x\frac{\partial\psi}{\partial x} - y\frac{\partial\psi}{\partial y}$ must have an invariable value

throughout the space. For a homogeneous phasis this condition is satisfied. And when therefore the given quantity of substance is homogeneously distributed through the space, we have a state of equilibrium. But if that state is to be realised the condition of stability must also be satisfied. From the principle that ψ must be a minimum, we derive for the condition of stability: [1]

$$\frac{\partial^2\psi}{\partial v^2}\,dv^2 + \frac{\partial^2\psi}{\partial x^2}\,dx^2 + \frac{\partial^2\psi}{\partial y^2}\,dy^2 + 2\,\frac{\partial^2\psi}{\partial x\,\partial v}\,dx\,dv +$$

$$+\,2\,\frac{\partial^2\psi}{\partial y\,\partial v}\,dy\,dv + 2\,\frac{\partial^2\psi}{\partial x\,\partial y}\,dx\,dy > 0 .$$

This condition can be brought under the following form: [2]

$$\frac{1}{\frac{\partial^2\psi}{\partial v^2}}\left\{\frac{\partial^2\psi}{\partial v^2}\,dv + \frac{\partial^2\psi}{\partial x\,\partial v}\,dx + \frac{\partial^2\psi}{\partial y\,\partial v}\,dy\right\}^2 + \left\{\frac{\partial^2\psi}{\partial x^2} - \frac{\left(\frac{\partial^2\psi}{\partial x\,\partial v}\right)}{\frac{\partial^2\psi}{\partial v^2}}\right\}dx^2 +$$

$$+\left\{\frac{\partial^2\psi}{\partial y^2} - \frac{\left(\frac{\partial^2\psi}{\partial y\,\partial v}\right)}{\frac{\partial^2\psi}{\partial v^2}}\right\}dy^2 + 2\left\{\frac{\partial^2\psi}{\partial x\,\partial y} - \frac{\frac{\partial^2\psi}{\partial x\,\partial v}\frac{\partial^2\psi}{\partial y\,\partial v}}{\frac{\partial^2\psi}{\partial v^2}}\right\}dx\,dy > 0 \quad . \ (3)$$

Now follows from:

$$\left(\frac{\partial\zeta}{\partial x}\right)_{pTy} = \left(\frac{\partial\psi}{\partial x}\right)_{vTy}$$

$$\left(\frac{\partial^2\zeta}{\partial x^2}\right)_{pTy} = \left(\frac{\partial^2\psi}{\partial x^2}\right)_{vTy} + \left(\frac{\partial^2\psi}{\partial x\,\partial v}\right)_{Ty}\left(\frac{dv}{dx}\right)_{pTy}$$

and from:

$$\left(\frac{\partial\psi}{\partial v}\right) = -p$$

follows

$$\left(\frac{\partial^2\psi}{\partial v\,\partial x} + \frac{\partial^2\psi}{\partial v^2}\frac{dv}{dx_p}\right) = 0$$

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[1] For a binary system the derivation of the condition of stability is given Cont. II p. 8. Before that time in Théor. Mol. Arch. Néerl. XXIV.

[2] See Arch. Néerl. Série II Tome II page 73.

Hence

$$\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{pTy} = \frac{\partial^2 \psi}{\partial x^2} - \frac{\left(\dfrac{\partial^2 \psi}{\partial x \, \partial v}\right)^2}{\dfrac{\partial^2 \psi}{\partial v^2}}.$$

In the same way we find

$$\left(\frac{\partial^2 \zeta}{\partial y^2}\right)_{pTx} = \frac{\partial^2 \psi}{\partial y^2} - \frac{\left(\dfrac{\partial^2 \psi}{\partial y \, \partial v}\right)^2}{\dfrac{\partial^2 \psi}{\partial v^2}}$$

and

$$\left(\frac{\partial^2 \zeta}{\partial x \, \partial y}\right)_{pT} = \frac{\partial^2 \psi}{\partial x \, \partial y} - \frac{\dfrac{\partial^2 \psi}{\partial x \, \partial v}\dfrac{\partial^2 \psi}{\partial y \, \partial v}}{\dfrac{\partial^2 \psi}{\partial v^2}}$$

So we can write (3) also under the following form:

$$\frac{1}{\dfrac{\partial^2 \psi}{\partial v^2}}\left\{\frac{\partial^2 \psi}{\partial v^2}\,dv + \frac{\partial^2 \psi}{\partial x \, \partial v}\,dx + \frac{\partial^2 \psi}{\partial y \, \partial v}\,dy\right\}^2 + \frac{\partial^2 \zeta}{\partial x^2}\,dx^2 + \frac{\partial^2 \zeta}{\partial y^2}\,dy^2 + 2\frac{\partial^2 \zeta}{\partial x \, \partial y}\,dx\,dy > 0$$

or

$$\frac{1}{\dfrac{\partial^2 \psi}{\partial v^2}}\left\{\frac{\partial^2 \psi}{\partial v^2}\,dv + \frac{\partial^2 \psi}{\partial x \, \partial v}\,dx + \frac{\partial^2 \psi}{\partial y \, \partial v}\,dy\right\}^2 + \frac{1}{\dfrac{\partial^2 \zeta}{\partial x^2}}\left\{\frac{\partial^2 \zeta}{\partial x^2}\,dx + \frac{\partial^2 \zeta}{\partial x \, \partial y}\,dy\right\}^2 +$$

$$+ dy^2 \left\{\frac{\partial^2 \zeta}{\partial y^2} - \frac{\left(\dfrac{\partial^2 \zeta}{\partial x \, \partial y}\right)^2}{\dfrac{\partial^2 \zeta}{\partial x^2}}\right\} > 0$$

In order to satisfy this last equation for every arbitrary value of dv, dx and dy, the following equation must be satisfied:

$$1^{st} \quad \frac{\partial^2 \psi}{\partial v^2} > 0 \ , \quad 2^{nd} \quad \frac{\partial^2 \zeta}{\partial x^2} > 0 \quad \text{and} \quad 3^{rd} \quad \frac{\partial^2 \zeta}{\partial x^2}\frac{\partial^2 \zeta}{\partial y^2} - \left(\frac{\partial^2 \zeta}{\partial x \, \partial y}\right)^2 > 0.$$

The form sub. 3$^{\text{rd}}$ or

$$\left\{\frac{\partial^2 \psi}{\partial x^2}\frac{\partial^2 \psi}{\partial v^2} - \left(\frac{\partial^2 \psi}{\partial x \, \partial v}\right)^2\right\}\left\{\frac{\partial^2 \psi}{\partial y^2}\frac{\partial^2 \psi}{\partial v^2} - \left(\frac{\partial^2 \psi}{\partial y \, \partial v}\right)^2\right\} - \left\{\frac{\partial^2 \psi}{\partial x \, \partial y}\frac{\partial^2 \psi}{\partial v^2} - \frac{\partial^2 \psi}{\partial x \, \partial v}\frac{\partial^2 \psi}{\partial y \, \partial v}\right\}^2 > 0$$

can be brought under the form:

$$\frac{\partial^2 \psi}{\partial v^2} \times \begin{vmatrix} \dfrac{\partial^2 \psi}{\partial v^2} & \dfrac{\partial^2 \psi}{\partial x\, \partial v} & \dfrac{\partial^2 \psi}{\partial y\, \partial v} \\[2ex] \dfrac{\partial^2 \psi}{\partial x\, \partial v} & \dfrac{\partial^2 \psi}{\partial x^2} & \dfrac{\partial^2 \psi}{\partial x\, \partial y} \\[2ex] \dfrac{\partial^2 \psi}{\partial y\, \partial v} & \dfrac{\partial^2 \psi}{\partial x\, \partial y} & \dfrac{\partial^2 \psi}{\partial y^2} \end{vmatrix} > 0 \quad \cdots \cdots \quad (4)$$

And we know from the theory of the quadric surfaces that if a relation exists between the coefficients as is indicated by the equation (4), such a surface is an ellipsoid. Coexisting phases being stable phases, the surface is a real ellipsoid, if C is positive.

If we bring through the line connecting the coexisting phases a plane cutting the tangent plane at the v, x, y-surface along a straight line and the surface of stability along an ellipse, then the directions of the nodal line and the before-mentioned straight line are conjugate directions for those elliptic sections. In the same way conjugate directions are the projection of these two lines on an arbitrary plane for the elliptic projection on that plane. If we give to the plane such a position that:

$$\frac{\partial^2 \psi}{\partial v^2}\, dv + \frac{\partial^2 \psi}{\partial x\, dv}\, dx + \frac{\partial^2 \psi}{\partial y\, dv}\, dy = 0$$

or what is the same $p = $ constant, then the factor of $v_2 - v_1$ is equal to zero, and we get after having eliminated dv_1 :

$$(x_2 - x_1)\left\{ \frac{\partial^2 \zeta}{\partial x_1^2}\, dx_1 + \frac{\partial^2 \zeta}{\partial x_1\, dy_1}\, dy_1 \right\} + (y_2 - y_1)\left\{ \frac{\partial^2 \zeta}{\partial x_1\, \partial y_1}\, dx_1 + \frac{\partial^2 \zeta}{\partial y_1^2}\, dy_1 \right\} = 0 \quad (5)$$

The projection on the xy-plane of the line connecting the coexisting phases, is therefore conjugate to the projection on that plane of the section of the tangent plane, indicated by $p = $ constant, with respect to the elliptic projection of the section of the surface of stability. This is the theorem which has been proved under another form Arch. Néerl. p. 76.

By giving such a position to the plane that

$$\frac{\partial^2 \psi}{\partial x\, \partial v}\, dv + \frac{\partial^2 \psi}{\partial x^2}\, dx + \frac{\partial^2 \psi}{\partial y\, \partial x}\, dy = 0$$

or $\dfrac{\partial \psi}{\partial x} =$ constant, we might derive an equation analogous to (5) for the y, v-surface; also for the x, v-surface by choosing the plane in such a way that:

$$\frac{\partial^2 \psi}{\partial y\, \partial v}\, dv + \frac{\partial^2 \psi}{\partial y\, \partial x}\, dx + \frac{\partial^2 \psi}{\partial y^2}\, dy = 0$$

or $\dfrac{\partial \psi}{\partial y} =$ is constant.

If we take volumes lying within the limits of the x, v, y-surface under consideration, which we shall henceforth call surface of coexistence, then the homogeneous phase thought in such a volume, will be stable, as long as

$$\frac{\partial^2 \psi}{\partial v^2} > 0 \ , \quad \frac{\partial^2 \zeta}{\partial x^2} = \frac{\partial^2 \psi}{\partial x^2} - \frac{\left(\dfrac{\partial^2 \psi}{\partial x\, \partial v}\right)^2}{\dfrac{\partial^2 \psi}{\partial v^2}} > 0 \text{ and } \frac{\partial^2 \zeta}{\partial y^2} - \frac{\left(\dfrac{\partial^2 \zeta}{\partial x\, \partial y}\right)^2}{\dfrac{\partial^2 \zeta}{\partial x^2}} > 0$$

In proportion as we move further from the sides of the surface of coexistence, we approach the volumes, for which $\dfrac{\partial p}{\partial v} = \dfrac{\partial^2 \psi}{\partial v^2} = 0.$

The surface, for which $\dfrac{\partial^2 \psi}{\partial v^2} = 0$, will for a ternary system take the place of the curve which we have represented by CKC' for a binary mixture in fig. 2 (previous communication).

But the stability will have ceased long before we have reached the volumes for which $\dfrac{\partial^2 \psi}{\partial v^2} = 0.$ For such volumes $\dfrac{\partial^2 \zeta}{\partial x^2} = - \infty$, whereas the condition of the stability is that this quantity be positive. Also $\dfrac{\partial^2 \zeta}{\partial y^2}$, which is equal to $\dfrac{\partial^2 \psi}{\partial y^2} - \dfrac{\left(\dfrac{\partial^2 \psi}{\partial y\, \partial v}\right)^2}{\dfrac{\partial^2 \psi}{\partial v^2}}$, would be $- \infty$ for such volumes, whereas the condition of stability is not only that this quantity be positive, but even that it have a value such that:

$$\frac{\partial^2 \zeta}{\partial y^2}\, \frac{\partial^2 \zeta}{\partial x^2} > \left(\frac{\partial^2 \zeta}{\partial x\, \partial y}\right)^2.$$

The conditions for stability increase therefore with the number

of components. For a simple substance a phasis is stable as long as

$$\frac{\partial^2 \psi}{\partial v^2} > 0.$$

For a binary mixture the following condition must be satisfied:

$$\frac{\partial^2 \psi}{\partial v^2} > \frac{\left(\frac{\partial^2 \psi}{\partial x\, \partial v}\right)^2}{\frac{\partial^2 \psi}{\partial x^2}}$$

for a ternary mixture the following condition must be satisfied:

$$\left\{\frac{\partial^2 \psi}{\partial v^2} - \frac{\left(\frac{\partial^2 \psi}{\partial x\, \partial v}\right)^2}{\frac{\partial^2 \psi}{\partial x^2}}\right\}\left\{\frac{\partial^2 \psi}{\partial v^2} - \frac{\left(\frac{\partial^2 \psi}{\partial y\, \partial v}\right)^2}{\frac{\partial^2 \psi}{\partial y^2}}\right\} > \left\{\frac{\partial^2 \psi}{\partial v^2} - \frac{\frac{\partial^2 \psi}{\partial x\, \partial v}\frac{\partial^2 \psi}{\partial y\, \partial v}}{\frac{\partial^2 \psi}{\partial x\, \partial y}}\right\}^2 \frac{\left(\frac{\partial^2 \psi}{\partial x\, \partial y}\right)^2}{\frac{\partial^2 \psi}{\partial x^2}\frac{\partial^2 \psi}{\partial y^2}}$$

The transition of the stable and unstable phases takes therefore place at

$$\frac{\partial^2 \psi}{\partial v^2} > 0 \,,\; \frac{\partial^2 \psi}{\partial v^2} - \frac{\left(\frac{\partial^2 \psi}{\partial x\, \partial v}\right)^2}{\frac{\partial^2 \psi}{\partial x^2}} > 0 \,,\; \frac{\partial^2 \psi}{\partial v^2} - \frac{\left(\frac{\partial^2 \psi}{\partial y\, \partial v}\right)^2}{\frac{\partial^2 \psi}{\partial y^2}} > 0$$

and

$$\begin{vmatrix} \dfrac{\partial^2 \psi}{\partial v^2}, & \dfrac{\partial^2 \psi}{\partial x\, \partial v}, & \dfrac{\partial^2 \psi}{\partial y\, \partial v} \\[2ex] \dfrac{\partial^2 \psi}{\partial v\, \partial x}, & \dfrac{\partial^2 \psi}{\partial x^2}, & \dfrac{\partial^2 \psi}{\partial y\, \partial x} \\[2ex] \dfrac{\partial^2 \psi}{\partial v\, \partial y}, & \dfrac{\partial^2 \psi}{\partial x\, \partial y}, & \dfrac{\partial^2 \psi}{\partial y^2} \end{vmatrix} = 0 \quad \cdots \cdots \text{(6)}$$

What the spinodal curve is for the binary mixture (see fig. 2 the curve $CEPE'C'$) the surface represented by (6) is for the ternary mixture, viz. the limit between the stable and unstable phases. In the sides of the prism described on the triangle oxy, this surface must therefore pass through the spinodal curves of the pairs of which the ternary system is composed. So we find from equation (6) which may be written:

37

$$\frac{\partial^2\psi}{\partial v^2}\frac{\partial^2\psi}{\partial x^2}\frac{\partial^2\psi}{\partial y^2} - \frac{\partial^2\psi}{\partial v^2}\left(\frac{\partial^2\psi}{\partial x\partial y}\right)^2 - \frac{\partial^2\psi}{\partial x^2}\left(\frac{\partial^2\psi}{\partial y\partial v}\right)^2 - \frac{\partial^2\psi}{\partial y^2}\left(\frac{\partial^2\psi}{\partial x\partial v}\right)^2 +$$

$$+ 2\frac{\partial^2\psi}{\partial x\partial y}\frac{\partial^2\psi}{\partial x\partial v}\frac{\partial^2\psi}{\partial y\partial v} = 0,$$

putting $\dfrac{\partial^2\psi}{\partial x^2} = \infty$ as it must be in the ovy coordinate plane:

$$\frac{\partial^2\psi}{\partial v^2}\frac{\partial^2\psi}{\partial y^2} - \left(\frac{\partial^2\psi}{\partial y\partial v}\right)^2 = 0.$$

But just as the spinodal curve for a binary mixture (fig. 7 and fig. 8) can have points in common with the curve $\dfrac{\partial^2\psi}{\partial v^2} = 0$, so it can also happen that the two surfaces corresponding to these curves have points in common for a ternary system. First of all they touch if $\dfrac{\partial^2\psi}{\partial v\,\partial x}$ and $\dfrac{\partial^2\psi}{\partial v\,\partial y}$ are both equal to zero — and in the second place they have points in common in the edges of the prism, so for the simple substances. And finally just as the spinodal curve and the connodal curve can have a point in common (the plaitpoint) for a binary system, in the same way the corresponding surfaces can have points in common for the ternary system, and touch each other in these points. For if for the second phasis we have:

$$v_2 = v_1 + dv_1 \quad x_2 = x_1 + dx_1 \text{ and } y_2 = y_1 + dy_1$$

the equation (1) becomes:

$$\frac{\partial^2\psi}{\partial v_1^2}dv_1^2 + \frac{\partial^2\psi}{\partial x_1^2}dx_1^2 + \frac{\partial^2\psi}{\partial y_1^2}dy_1^2 + 2\frac{\partial^2\psi}{\partial v_1\,\partial x_1}dv_1\,dx_1 +$$

$$+ 2\frac{\partial^2\psi}{\partial v_1\,\partial y_1}dv_1\,dy_1 + 2\frac{\partial^2\psi}{\partial x_1\,\partial y_1}dx_1\,dy_1 = 0$$

or

$$\frac{\left\{\dfrac{\partial^2\psi}{\partial v_1^2}dv_1+\dfrac{\partial^2\psi}{\partial x_1\,\partial v_1}dx_1+\dfrac{\partial^2\psi}{\partial y_1\,\partial v_1}dy_1\right\}^2}{\dfrac{\partial^2\psi}{\partial v_1^2}}+$$

$$+\frac{\left\{\left[\dfrac{\partial^2\psi}{\partial x_1^2}-\dfrac{\left(\dfrac{\partial^2\psi}{\partial x_1\,\partial v_1}\right)^2}{\dfrac{\partial^2\psi}{\partial v_1^2}}\right]dx_1+\left[\dfrac{\partial^2\psi}{\partial x_1\partial y_1}-\dfrac{\dfrac{\partial^2\psi}{\partial x_1\,\partial v_1}\dfrac{\partial^2\psi}{\partial y_1\,\partial v_1}}{\dfrac{\partial^2\psi}{\partial v_1^2}}\right]dy_1\right\}^2}{\dfrac{\partial^2\psi}{\partial x_1^2}-\dfrac{\left(\dfrac{\partial^2\psi}{\partial x_1\,\partial v_1}\right)^2}{\dfrac{\partial^2\psi}{\partial v_1^2}}}+$$

$$+dy_1^2\left\{\left[\dfrac{\partial^2\psi}{\partial y_1^2}-\dfrac{\left(\dfrac{\partial^2\psi}{\partial y_1\,\partial v_1}\right)^2}{\dfrac{\partial^2\psi}{\partial v_1^2}}\right]-\dfrac{\left[\dfrac{\partial^2\psi}{\partial x_1\partial y_1}-\dfrac{\dfrac{\partial^2\psi}{\partial v_1\partial x_1}\dfrac{\partial^2\psi}{\partial v_1\partial y_1}}{\dfrac{\partial^2\psi}{\partial v_1^2}}\right]^2}{\dfrac{\partial^2\psi}{\partial x_1^2}-\dfrac{\left(\dfrac{\partial\psi}{\partial x_1\,\partial v_1}\right)^2}{\dfrac{\partial^2\psi}{\partial v_1^2}}}\right\}=0$$

$\dfrac{\partial^2\psi}{\partial v_1^2}dv_1+\dfrac{\partial^2\psi}{\partial v_1\,\partial x_1}dx_1+\dfrac{\partial^2\psi}{\partial v_1\,\partial y_1}dy_1$ being equal to $-dp$, and the

numerator of the second term being equal to $d\left(\dfrac{\partial\zeta}{\partial x}\right)_p$, and as p and

$\dfrac{\partial\zeta}{\partial x}$ must be equally great for coexisting phases, the above equation cannot be satisfied without the factor of dy_1^2 being 0. As we saw before, we reduce this factor to the criterion for the limit of the unstable and stable phases; and the surface of coexistence and the spinodal surface have therefore an element in common.

As a rule these two surfaces will not only touch each other in one point, but we shall be able to give a continuous series of points of contact, so a curve along which the surface of coexistence envelopes the spinodal surface. The latter case has already been discussed in our former communication, when at equal temperature and variable pressure every time another mixture was in plaitpoint circumstance. The case that they touch each other only in one point occurs when we can form a mixture of the three components

37*

for which T_{cr} is a minimum. But it may be advisable to wait with the discussion of this and similar cases till an experimental investigation has brought them to light.

If by increase of temperature the surface of coexistence has so far contracted that it no longer covers the whole triangle oxy, a tangent cylindre may be drawn normal to the xy-surface. All the points, in which the tangent cylindre and the surface of coexistence touch, represent mixtures which are in critical tangent-point circumstance. A plaitpoint can never lie on this apparent circumference of the surface of coexistence, except in some special cases. For as the generatrices of this tangent cylindre are parallel to the volume-axis and p must have the same value for the pair of phases coinciding in a plaitpoint, we have

$$\frac{\partial^2 \psi}{\partial v^2} = 0$$

for such a special case. In order not to have $\dfrac{\partial^2 \zeta}{\partial x_1^2}$ or $\dfrac{\partial^2 \zeta}{\partial y_1^2}$ negative, $\dfrac{\partial^2 \psi}{\partial x\, \partial v}$ and $\dfrac{\partial^2 \psi}{\partial y\, \partial v}$ must be equal to 0. Such a mixture behaves as a simple substance even under critical circumstances. See for a similar circumstance with a binary system Cont. II page 116. So the plaitpoints lie either on the liquid sheet, or on the vapour sheet of the surface of coexistence. In the first case all mixtures, indicated by points of the xy-surface, lying between the section of the tangent cylindre and the projection of the curve on which the plaitpoints are situated, have retograde condensation of the first kind. If the plaitpoints lie on the vapour sheet, then such mixtures have r. c. II.

(To be continued).

Physics. — *"On the asymmetry of the electro-capillary-curve."* By Dr. J. J. VAN LAAR (communicated by Prof. VAN DER WAALS).

I. We may suppose, that it is well known, that the new theory of the so called *Capillary-Electrometer* of LIPPMANN may be described as follows.

Two mercury surfaces, one large (A), the other small (B) — this latter in the so called capillary — are separated by a conductive liquid C, diluted H_2SO_4, a solution of K Cl, or any other solution. In all