Physics. — *"Contribution to the theory of binary mixtures, II"*, by Prof. J. D. VAN DER WAALS. (Continued, see p. 621).

Not to suspend too long the description of the course of the q-lines in the case that the locus $\frac{d^2\psi}{dx^2}=0$ exists, we shall postpone the determination of the temperature at which this locus has disappeared, and the inquiry into the value of x and v for the point at which it disappears — and proceed to indicate the modification in the course of the q-lines which is the consequence of its existence.

From the value of $\frac{dv}{dx_q} = -\frac{\frac{d^2\psi}{dx^2}}{\frac{d^2\psi}{dxdv}}$ follows that when a q-line passes through the curve $\frac{d^2\psi}{dx^2}=0$, it has a direction parallel to the

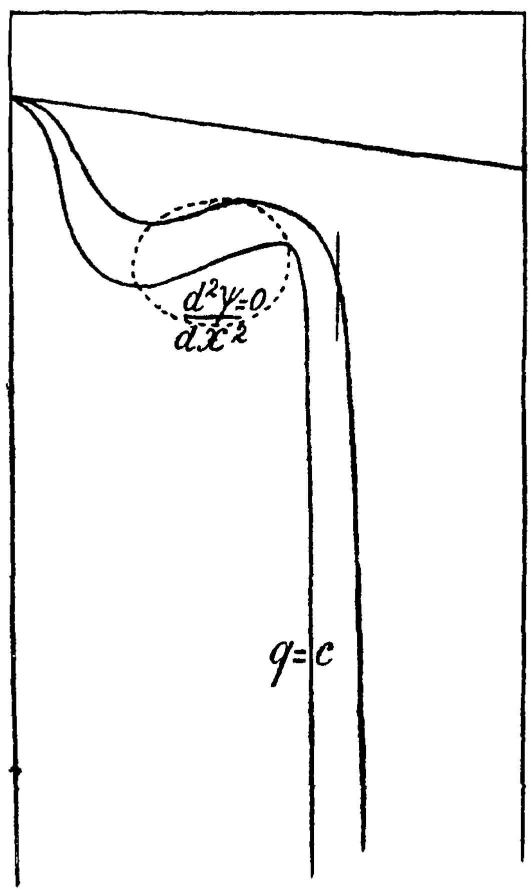

Fig. 3.

x-axis in such a point of intersection. So a q-line meeting $\frac{d^2\psi}{dx^2}=0$, will be twice directed parallel to the x-axis, and have a shape as represented in fig. 3 — at least as long as the curve $\frac{d^2\psi}{dxdv}=\left(\frac{dp}{dx}\right)_v=0$ does not occur. Such a shape may. therefore, be found for the q-lines, in the case that the second component has a higher value of b, and lower value of T_k —, and such a shape will certainly present itself in the case mentioned when the temperature is low enough.

Then there is a group of q-lines, for which maximum volume, and minimum volume is found. The outmost line on one side of this group of q-lines, viz. that for which q possesses the highest value, is that for which maximum and minimum volume have coincided, and which touches the curve $\frac{d^2\psi}{dx^2}=0$ in the point, in which this curve itself has the smallest volume. The other outmost line of this group of q-lines, viz. that for which q possesses the smallest value, is that for which again maximum and minimum volume have coincided, and which also touches the curve $\frac{d^2\psi}{dx^2}=0$, but in that point in which this curve itself has its largest volume. So for these two points of contact the equation $\frac{d^3\psi}{dx^3}=0$ holds. These two points of contact are, therefore, found by examining where the curves $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^3\psi}{dx^3}=0$ intersect. This last locus appears to be independent of the temperature, as we may put $\frac{d^3a}{dx^3}$ equal to 0. We find from the equation on p. 638

$$\frac{d^3\psi}{dx^3}=MRT\left\{-\frac{1-2x}{x^2(1-x)^2}+2\frac{\left(\frac{db}{dx}\right)^3}{(v-b)^3}+\frac{\frac{d^2b}{dx^2}}{(v-b)^2}\right\}=0.$$

If we neglect $\frac{d^2b}{dx^2}$, we find from $\frac{d^3\psi}{dx^3}=0$

$$\frac{\frac{db}{dx}}{v-b}=\sqrt[3]{\frac{1-2x}{2x^2(1-x)^2}}.$$

The locus $\frac{d^3\psi}{dx^3}=0$ occurs, therefore, only in the left side of the figure or for values of x below $\frac{1}{2}$. The line $x={}^1/_2$ is an asymptote for this curve, and only at infinite volume this value of x is reached.

And as for $x=0$ also $v-b$ must be $=0$, the curve $\frac{d^3\psi}{dx^3}=0$ starts from the same point from which all the q-lines start. If $\frac{d^2b}{dx^2}$ should not be equal to 0, we have ground for putting this quantity positive (Cont. II, p. 21), and we arrive at the same result for the initial point and the final point of the curve $\frac{d^3\psi}{dx^3}=0$.

So the points of the curve $\frac{d^2\psi}{dx^2}=0$, where tangents may be drawn to it parallel to the x-axis, lie certainly at values of x smaller than $\frac{1}{2}$, and accordingly the two outer ones of the group of the q-lines with maximum and minimum volume have their horizontal tangents also in the left side of the figure. The q-line with the highest value of q at lower value of x than that with the lowest value. This is represented in fig. 4.

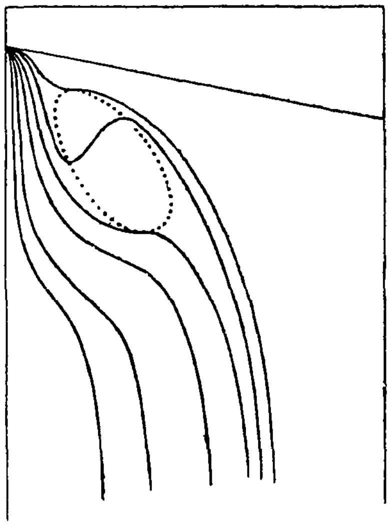

Fig. 4.

We notice at the same time that the points in which a q-line touches the curve $\frac{d^2\psi}{dx^2}=0$, are points of inflection for such a q-line, just as this is the case with the p-lines when a p-line touches the curve $\frac{d^2\psi}{dv^2}$. From

$$q=\left(\frac{d\psi}{dx}\right)_v$$

follows:

$$\frac{d^2\psi}{dxdv}\left(\frac{dv}{dx}\right)_q+\frac{d^2\psi}{dx^2}=0,$$

and

$$\frac{d^2\psi}{dxdv}\frac{d^2v}{dx^2}_q+\left\{\frac{d^3\psi}{dxdv^2}\left(\frac{dv}{dx}\right)_q^2+2\frac{d^3\psi}{dx^2dv}\left(\frac{dv}{dx}\right)_q+\frac{d^3\psi}{dx^3}\right\}=0.$$

In the points mentioned $\left(\frac{dv}{dx}\right)_q=0$, because $\frac{d^2\psi}{dx^2}=0$, and at the same time $\frac{d^3\psi}{dx^3} = 0$. Hence $\left(\frac{d^2v}{dx^2}\right)_q = 0$, which appears also immediately from the figure.

Within the curve $\frac{d^2\psi}{dx^2} = 0$ every q-line that intersects it, has also a point of inflection, because the latter must pass from minimum volume to maximum volume in its course. So there is a continuous series of points in which q-lines possess points of inflection between the two points in which horizontal tangents may be drawn to $\frac{d^2\psi}{dx^2} = 0$. But there is also a continuous series of points in which the q-lines must possess points of inflection on the left of the curve $\frac{d^2\psi}{dx^2} = 0$, so with smaller value of x. For every q-line has its convex side turned to the x-axis just after it has left the starting point. If it is to enter the curve $\frac{d^2\psi}{dx^2} = 0$ in horizontal direction and to pass then to smaller volume, it must turn its concave side to the x-axis in that point, and so it must have previously possessed a point of inflection. Most probably the last-mentioned branch is somewhere continuously joined to the first mentioned one. If so, there is a closed curve in which $\frac{d^2v}{dx^2}_q = 0$ — and then it may be expected that this closed curve contracts with rise of T, and has disappeared above a certain temperature. But these and other particulars may be left to a later investigation.

We have now described the shape of the q-lines, 1. in the case that neither $\frac{d^2\psi}{dx^2}$, nor $\frac{d^2\psi}{dxdv}$ is equal to 0, 2. in the case that the curve $\frac{d^2\psi}{dxdv} = 0$ exists, 3. in the case that the curve $\frac{d^2\psi}{dx^2} = 0$ is found. It remains to examine the course of the q-lines when both curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dxdv} = 0$ exist.

For the occurrence of the $\frac{d^2\psi}{dx^2} = 0$ it is only required that $\frac{d^2a}{dx^2}$ be positive, as we shall always suppose, and that T is below the value of the temperature at which the curve $\frac{d^2\psi}{dx^2} = 0$ has contracted to a single point. It may, therefore, occur with every binary system, without our having to pay attention to the choice of the components.

But the occurrence of the curve $\frac{d^2\psi}{dx dv}=\left(\frac{dp}{dx}\right)_v=0$ is not always possible, as we already showed in the discussion of the shape of the isobars. If we consult fig. 1 (These Proc. IX p. 630) it appears that the curve $\left(\frac{dp}{dx}\right)_v=0$ does not exist throughout the whole width of the diagram of isobars.

With mixtures for which the course of the isobars is, as is the case in the left side of the figure, the line $\left(\frac{dp}{dx}\right)_v=0$ does not exist at all. Only with mixtures for which the course of the isobars is represented by the middle part of fig. 1 it exists and if the asymptote is found, it can occur with all kinds of volumes. Also with mixtures for which the course of the isobars is represented by the right part of fig. 1, it exists, but then only at very small volumes, and it possesses only the branch which approaches the line $v=b$ asymptotically.

Let us now consider a mixture such that the curve $\left(\frac{dp}{dx}\right)_v=0$ is really present at such a temperature that also the curve $\frac{d^2\psi}{dx^2}=0$ exists; then we have still to distinguish between two cases, i. e. 1. when the two loci mentioned do not intersect, and 2. when they do intersect. If they do not intersect, and the curve $\left(\frac{dp}{dx}\right)_v=0$ lies on the right of $\frac{d^2\psi}{dx^2}=0$, then the q-line, after having had its maximum and minimum volume, will intersect the line $\left(\frac{dp}{dx}\right)_v=0$, in that point of intersection will have a tangent // v-axis; it will further run back to smaller volume, just as this is the case with one of the q-lines drawn in fig. 2. This may e.g. occur for mixtures corresponding to the left region of the diagram of isobars, when this region is so wide that also the asymptote and a further part of the curve $\left(\frac{dp}{dx}\right)_v=0$ is found. If with non-intersection the relative position of the two curves $\frac{d^2\psi}{dx^2}=0$ and $\left(\frac{dp}{dx}\right)_v=0$ are reversed, this can probably not occur but for mixtures which correspond to a region of the diagram of isobars which has been chosen far on the right side. The course of the q-lines which then pass through the curve $\frac{d^2\psi}{dx^2}=0$, is represented in fig. 5. But when the two

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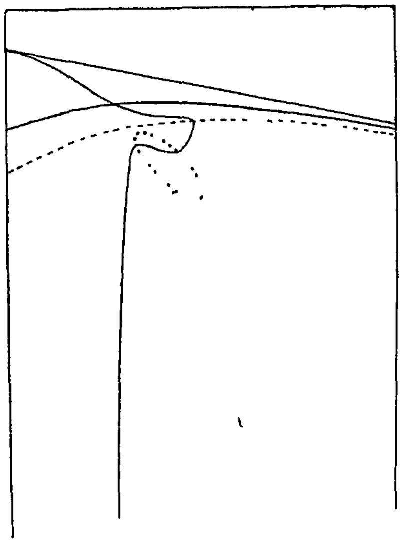

Fig. 5.

curves $\frac{d^2\psi}{dx^2}=0$ and $\left(\frac{dp}{dx}\right)_v=0$ intersect, which then necessarily takes place in 2 points, the shape of the q-lines is much more intricate. Then numerator and denominator are equal to zero in

$$\left(\frac{dv}{dx}\right)_q = \frac{\frac{d^2\psi}{dx^2}}{\left(\frac{dp}{dx}\right)_v}\text{, and } \left(\frac{dv}{dx}\right)_q \text{ is not}$$

to be determined from this equation. Then $\left(\frac{dv}{dx}\right)_q$ must be determined from :

$$\left(\frac{d^3\psi}{dxdv^2}\right)\left(\frac{dv}{dx}\right)_q^2 + 2\left(\frac{d^3\psi}{dx^2dv}\right)\left(\frac{dv}{dx}\right)_q + \left(\frac{d^3\psi}{dx^3}\right) = 0.$$

In the discussion of the shape of the p-lines we came across an analogous case when the curves $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^2\psi}{dxdv}=0$ intersect; and there we found that the two points of intersection had a different character. For one point of intersection the p-line has two different real directions, depending on the sign of $\frac{d^3\psi}{dv^3}\frac{d^3\psi}{dvdx^2}-\left(\frac{d^3\psi}{dxdv^2}\right)^2$. If this expression was negative, the loop-isobar passed through that point of intersection. In the same way, when from the above quadratic equation for $\left(\frac{dv}{dx}\right)_q$ we write the condition on which the roots are real, we find the condition :

$$\left[\frac{d^3\psi}{dx^3}\frac{d^3\psi}{dxdv^2}-\left(\frac{d^3\psi}{dx^2dv}\right)^2\right] \text{negative;}$$

which may be immediately found from the condition for the loop of the *loop-isobar*, as requirement for the loop of the *loop-q-line*, when we interchange x and v.

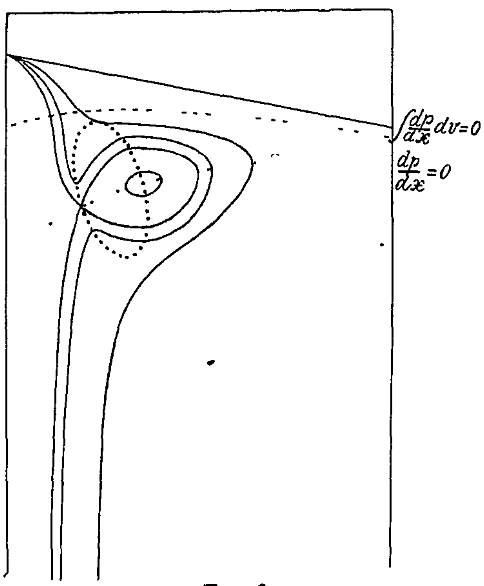

Fig. 6.

The q-line which passes through the first point where the above condition is negative, has, therefore, a real double point, and runs round the other point of intersection before passing through this double point for the second time. In Fig. 6 the dotted closed curve $\frac{d^3\psi}{dx^2}=0$ has been traced, and also the dotted curve $\left(\frac{dp}{dx}\right)=-\left(\frac{d^2\psi}{dvdx}\right)=0$. The point of intersection lying on the left, is the double point. According to what was stated before, $\frac{d^3\psi}{dx^3}$ is negative in this point, and the quantity $\frac{d^3\psi}{dxdv^2}$ is positive, which is also to be deduced from what was mentioned previously about the sign of $\frac{d^2p}{dxdv}=-\frac{d^3\psi}{dxdv^2}$. So the criterion by which the reality of the two directions of $\left(\frac{dv}{dx}\right)_q$ is tested is satisfied in that point of intersection. In the second point of intersection $\frac{d^3\psi}{dx^3}$ is positive, and $\frac{d^3\psi}{dxdv^3}$ is also positive. It is true that it does not follow from this that $\frac{d^3\psi}{dx^2}\frac{d^3\psi}{dxdv^2}>\left(\frac{d^3\psi}{dvdx^2}\right)^2$ — but 1 it appears in the drawing of the loop-q-line that there is no other possibility but that it runs round the second point of intersection, and 2 it appears, that just as we have mentioned in the analogous case for the shape of the p-lines (Footnote p. 626), only when the two points of intersection coincide, so when the two curves $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dxdv}=0$ touch, the quantity $\frac{d^3\psi}{dx^3}\frac{d^3\psi}{dxdv^2}-\left(\frac{d^3\psi}{dvdx^2}\right)^2$ is equal to 0. In the case that $\frac{d^2\psi}{dx^2}=0$ has greater dimensions, so at lower temperature, the loop-q-line will, of course, extend still much more to the right, and the higher q-lines must be strongly compressed at the point where the curve $\left(\frac{dp}{dx}\right)_v=0$ cuts the second axis (the line $x=1$).

This loop-q-line determines the course of all the other q-lines. Thus in fig. 6 a somewhat higher q-line passes through $\frac{d^2\psi}{dx^2}=0$, in vertical direction just above the double point, rises then till it

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passes through this curve for the second time, reaches its highest point, after which it meets the curve $\left(\frac{dp}{dx}\right)_v = 0$ in vertical direction, and then pursues its course downward after having been directed horizontally twice more.

It must then again approach asymptotically that value of x, at which it intersected the line $\int \frac{dp}{dx}\, dv = 0$ shortly after the beginning of its course. This line has also been drawn in fig. 6. It is evident that it may not intersect the curve $\frac{d^2\psi}{dx^2} = 0$. In fig. 6 it has, accordingly, remained restricted to smaller volumes than those of the curve $\frac{d^2\psi}{dx^2} = 0$. For the assumption of intersection involves that a q-line could meet the locus $\int \frac{dp}{dx}\, dv = 0$ several times. As $q = MRT\, l\frac{x}{1-x}$ in such a meeting point, it follows from this that only one value of x can belong to given q. It deserves notice that in this way without any calculation we can state this thesis: "The curves $\frac{d^2\psi}{dx^2} = 0$ and $\int \frac{dp}{dx}\, dv = 0$ can never intersect." According to the equation of state it would run like this: "The equations:

$$MRT \left\{\frac{1}{x(1-x)} + \frac{\left(\frac{db}{dx}\right)^2}{(v-b)^2}\right\} = \frac{\frac{d^2a}{dx^2}}{v} \text{ and } \frac{MRT\frac{db}{dx}}{v-b} = \frac{\frac{da}{dx}}{v}$$

can have no solution in common. Indeed, if v from the second equation is expressed in x and T, and if this value is substituted in the first equation, we get the following quadratic equation in MRT:

$$(MRT)^2 \left\{\frac{1}{x(1-x)} + \frac{1}{b^2}\left(\frac{db}{dx}\right)^2 + \frac{1}{b}\frac{db}{dx}\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}\right\} -$$

$$- 2(MRT)\left\{\frac{1}{b^2}\frac{db}{dx}\frac{da}{dx} - \frac{1}{b}\frac{1}{2}\frac{d^2a}{dx^2}\right\} + \frac{1}{b^2}\left(\frac{da}{da}\right)^2 = 0.$$

A value of MRT, which must necessarily be positive to have significance, requires $\frac{1}{b^2}\frac{db}{dx}\frac{da}{dx} > \frac{1}{2b}\frac{d^2a}{dx^2}$. From the foregoing remarks it is sufficiently clear that $\frac{da}{dx}$ must be positive to render the locus $\int \frac{dp}{dx}\,dv = 0$ possible, and that $\frac{d^2a}{dx^2}$ must be positive to render $\frac{d^2\psi}{dx^2} = 0$ possible. The roots of the given quadratic equation, however, are then imaginary, the square of $\frac{1}{b^2}\frac{db}{dx}\frac{da}{dx} - \frac{1}{2b}\frac{d^2a}{dx^2}$ being necessarily smaller than the square of $\frac{1}{b^2}\frac{db}{dx}\frac{da}{dx}$, and the square of this being smaller than the product of $\frac{1}{b^2}\left(\frac{da}{dx}\right)^2$ and the factor of (MRT).

But let us return to the description of the course of the remaining q-lines. There is, of course, a highest q-line, which only touches the locus $\frac{d^2\psi}{dx^2} = 0$, directed horizontally in that point of contact, and for which also $\frac{d^3\psi}{dx^3} = 0$ in that point. There is also a q-line which touches the locus $\frac{d^2\psi}{dx^2} = 0$ in its downmost point, and which as a rule will be another than that which touches it in its highest point. The q-lines of higher degree than the higher of these two have again the simple course which we have traced in fig. 2 (p. 635) for that q-line which intersects the locus $\left(\frac{dp}{dx}\right)_v = 0$. Only through their considerable widening all of them will more or less evince the influence of the existence of the above described complication. The q-lines of lower degree than the loop-q-line have split up into two parts, one part lying on the left which shows the normal course of a q-line which cuts $\left(\frac{dp}{dv}\right)_v = 0$; and a detached closed part which remains enclosed within the loop. Such a closed part runs round the second point of intersection which $\left(\frac{dp}{dx}\right)_v = 0$ and $\frac{d^2\psi}{dx^2} = 0$ have in common, passes in its lowest and highest point through $\frac{d^2\psi}{dx^2} = 0$, and through $\left(\frac{dp}{dx}\right)_v = 0$ in the point lying most to the right and most to the left. With continued decrease of the degree of q this detached part contracts, and disappears as isolated point. This takes place before q has descended to negative infinite, so that q-lines of very low degree have entirely resumed the simple course which such lines have when only the curve $\left(\frac{dp}{dx}\right)_v = 0$ exists.

Also in this general case for the course of the q-lines we can form an opinion about the locus of the points of inflection of these curves, so of the points in which $\left(\frac{d^2v}{dx^2}\right)_q = 0$. We already mentioned above that when the line $\left(\frac{dp}{dx}\right)_v = 0$ exists at a certain distance from it there must be points of inflection on the q-lines at larger volume. If also the asymptote of $\left(\frac{dp}{dx}\right)_v = 0$ should exist, also this series of points of inflection of the q-lines has evidently the same asymptote. In fig. 6 this asymptote lies outside the figure, and so it is not represented — but the remaining part is represented, modified, however, in its shape by the existence of the double point. The said series of points of inflection is now sooner to be considered as consisting of two series which meet in the double point, and which have, therefore, got into the immediate neighbourhood of the line $\left(\frac{dp}{dx}\right)_v = 0$ there. So there comes a series from the left, which as it approaches the double point, draws nearer to $\left(\frac{dp}{dx}\right)_v = 0$, and from the double point there goes a series to the right, which first remains within the space in which $\frac{d^2\psi}{dx^2} = 0$ is found, and which passes through the lowest point of this curve, but then moves further to the side of the second component at larger volume than that of the curve $\left(\frac{dp}{dx}\right)_v = 0$. The double point of the q-loop-line is, therefore, also double point for the locus of the points of inflection of the q-lines, and the continuation of the two branches which we mentioned above, must be found above the curve $\left(\frac{dp}{dx}\right)_v = 0$. Accordingly, we have there a right branch, which runs within $\frac{d^2\psi}{dx^2} = 0$, and passes through the highest point of this curve, and a left branch which from the double point runs to the left of the loop-q-line, and probably merges into the preceding branch. If this is the case the outmost q-lines on the two sides, both that lying very low and that lying very high, have no points of inflection.

THE SPINODAL CURVE AND THE PLAITPOINTS.

The spinodal curve is the locus of the points in which a p- and a q-line meet. In these points $\frac{dv}{dx_p} = \frac{dv}{dx_q}$ and so $-\frac{\frac{d^2\psi}{dxdv}}{\frac{d^2\psi}{dv^2}} = -\frac{\frac{d^2\psi}{dx^2}}{\frac{d^2\psi}{dxdv}}$ or $\frac{d^2\psi}{dv^2}\frac{d^2\psi}{dx^2} = \left(\frac{d^2\psi}{dxdx}\right)^2$. In order to judge about the existence of such points of contact, we shall have to trace the p and the q lines together. As appears from fig. 1 p. 630 the shape of the p-lines is very different according as a region is chosen lying on the left side, or in the middle or on the right side; but the course of the q-lines in the different regions is in so far independent of the choice of the regions that $q_{-\infty}$ always represents the series of the possible volumes of the first component, and $q_{+\infty}$ the series of the possible volumes of the second component, and also the line of the limiting volumes. As the shape of the p-lines can be so very different we shall not be able to represent the shape of the spinodal line by a single figure. Besides the course of the p-lines depends on the existence or non-existence of the curve $-\frac{dp}{dv} = \frac{d^2\psi}{dv^2} = 0$, and the course of the q-lines on the existence or non-existence of the curve $\frac{d^2\psi}{dx^2} = 0$, and besides, and this holds for both, on the existence of the curve $\frac{d^2\psi}{dxdv} = 0$. Hence if for all possible cases we would illustrate the course of the spinodal curve in details by figures, this examination would become too lengthy. We shall, therefore, have to restrict ourselves, and try to discuss at least the main points.

Let us for this purpose choose in the first place a region from the left side of the general p-figure, and let us think the temperature so low, so below $(T_k)_2$, that there are still two isolated branches for the curve $\frac{dp}{dv} = 0$ all over the width of the region.

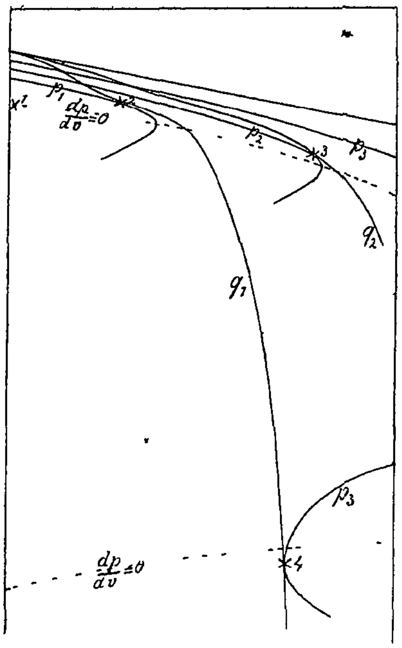

Fig. 7.

In fig. 7 T is thought higher than the temperature at which $\frac{d^2\psi}{dx^2}=0$ vanishes, and in fig. 8 below this temperature. In fig. 7 all the q-lines have the very simple course which we previously indicated for them, and the p-lines the well-known course, with which $\left(\frac{dv}{dx}\right)_p$ is positive on the liquid side of $\frac{dp}{dv}=0$, and on the vapour side of $\frac{dp}{dv}=0$, negative between the two branches of this curve, the transition of $\left(\frac{dv}{dx}\right)_p$ from positive to negative taking place through infinitely large. The isobars p_1, p_2 and p_3 have been indicated in the figure, in which $p_1 < p_2 < p_3$. Also a few q-lines, $q_1 < q_2$ and the points of contact of p_1 to q_1 and of p_3 to q_2. Also on the vapour side a point of contact of p_3 to q_1. It is clear 1[st] that every q-line yields two points for the spinodal curve, and 2[nd] that these points of contact lie outside the region in which $\frac{dp}{dv}$ is positive. On the other hand we see that the distance from the spinodal curve to the curve $\frac{dp}{dv}=0$ can be nowhere very large. Only by drawing very accurately it can be made evident that on the vapour side the spinodal curve has always a somewhat larger volume than the vapour branch of the curve $\frac{dp}{dv}=0$. In the four points, in which $\frac{dp}{dv}=0$ intersects the sides, indeed, the spinodal line coincides with this curve.

Fig. 7*b* has been drawn to give an insight into the circumstances at the plaitpoint. At $T > (T_k)_2$ the two branches of the curve $\frac{dp}{dv}=0$ have united at that value of x, for which $T=(T_k)_x$. One of the p-lines, namely that of the value $p=(p_k)_x$, touches in the point at which the two branches have joined at a volume $v = (v_k)_x$, and has a point of inflection there. Two parts of q-lines have been drawn as touching the p-line. The two points of contact (1) and (2) are points of the spinodal curve, and lie again outside the curve $\frac{dp}{dv} = 0$. For a higher p-line these points will come closer together. And the place where they coincide is the plaitpoint. As in point (1) $\left(\frac{d^2v}{dx^2}\right)_p > \left(\frac{d^2v}{dx^2}\right)_q$ and reversely in point(2) $\left(\frac{d^2v}{dx^2}\right)_q > \left(\frac{d^2v}{dx^2}\right)_p$, $\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q$ when (1) and (2)

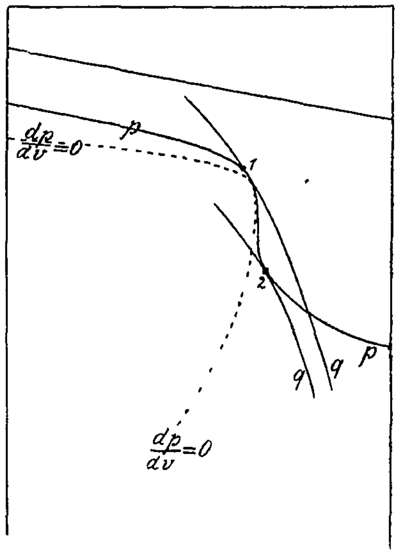

Fig. 7b.

have coincided, and this may be considered as the criterion for the plaitpoint so that in such a point the two equations:

$$\left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q$$

and

$$\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q.$$

hold.

The following remark may not be superfluous. In point (2) $\left(\frac{d^2v}{dx^2}\right)_p$ is not only smaller than $\left(\frac{d^2v}{dx^2}\right)_q$, but even negative. In order to find the plaitpoint, the point in which 2 points of contact for the q and the p-lines coincide, and so $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ have the same value, $\left(\frac{d^2v}{dx^2}\right)_p$ must first reverse its sign in the point (2) with increase of the value of p for the isobar before the equality with $\left(\frac{d^2v}{dx^2}\right)_q$ can be obtained. And that, at least in this case, this reversal of sign must take place with point (2) and not with point (1), appears from the positive value of $\left(\frac{d^2v}{dx^2}\right)_q$. So we arrive here at the already known theses that in the plaitpoint the isobar surrounds the spinodal curve, and also the binodal one.

As

$$dv_p = \left(\frac{dv}{dx}\right)_p dx + \frac{1}{1.2}\left(\frac{d^2v}{dx^2}\right)_p dx^2 + \frac{1}{1.2.3}\left(\frac{d^3v}{dx^3}\right)_p dx^3 \text{ etc.}$$

and

$$dv_q = \left(\frac{dv}{dx}\right)_q dx + \frac{1}{1.2}\left(\frac{d^2v}{dx^2}\right)_q dx^2 + \frac{1}{1.2.3}\left(\frac{d^3v}{dx^3}\right)_q dx^3 \text{ etc.}$$

we find for a plaitpoint:

$$dv_p - dv_q = \frac{1}{1.2.3}\left\{\left(\frac{d^3v}{dx^3}\right)_p - \left(\frac{d^3v}{dx^3}\right)_q\right\} dx^3 \text{ etc.}$$

So the p- and the q-lines meet and intersect in a plaitpoint, and this is not always changed when a point should be a double plaitpoint. We shall, namely, see later on that the criterion for a double plaitpoint is sometimes as follows:

$$\left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q$$

and

$$\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q = 0.$$

Let us now proceed to the discussion of the case represented by fig. 8. Here it is assumed that T lies below the temperature at which $\frac{d^2\psi}{dx^2} = 0$ vanishes, so that this locus exists, it being moreover supposed that it intersects the curve $\frac{dp}{dv} = 0$. It appears from the drawing that for the q-lines for which maximum and minimum volume occurs, two new points of contact with the p-lines are necessarily found in the neighbourhood of the points of largest and smallest volumes at least for so far as these points lie on the liquid side of $\frac{dp}{dv} = 0$.

So there is a group of q-lines on which 4 points of the spinodal curve occur, and which will therefore intersect the spinodal curve in 4 points. The two new points of contact lie on either side of $\frac{d^2\psi}{dx^2} = 0$, and these two new points of contact do not move far away from this curve, the two old points of contact not being far removed from $\frac{dp}{dv} = 0$.

If we raise the value of q, the two new points of contact draw nearer to each other. Thus e.g. the q-line which touches $\frac{d^2\psi}{dx^2}$ in its highest point, and for which $\left(\frac{dv}{dx}\right)_q = 0$ and also $\left(\frac{d^2v}{dx^2}\right)_q = 0$ in that point has also been drawn in the figure. Also this q-line may still be touched by two different p-lines, which, however, have not been represented in the drawing. For a still higher q-line these points would coincide, and in consequence of the coincidence of two points of the spinodal curve a plaitpoint would then be formed. $\left(\frac{d^2v}{dx^2}\right)_v$ always being positive, $\left(\frac{d^2v}{dx^2}\right)_q$, which has been negative for a long time in the point lying on the left side, must first reverse its sign before it can coincide with the point lying on the right — a remark analogous to that which we made for the plaitpoint that we discussed above.

If on the other hand the value of q is made to descend, the point of contact lying most to the left will move further and further from the curve $\frac{d^2\psi}{dx^2}=0$, and nearer and nearer to the curve $\frac{dp}{dv}=0$, till for q-lines of very low degree, for which as we shall presently see, the number of points of contact has again descended to two, the whole bears the character of a point of contact lying on the liquid side.

But something special may be remarked about the two inner points of contact of the four found on the above q-line. When the q-line descends in degree, these points will approach each other, and they will coincide on a certain q-line. Then we have again a plaitpoint. In this case neither $\left(\frac{d^2v}{dx^2}\right)_q$, nor $\left(\frac{d^2v}{dx^2}\right)_p$ need reverse its sign because these quantities have always the same sign for each of the two points of contact which have not yet coincided, i. e. in this case the positive sign. But in this case, too, there is again besides contact, also intersection of the p- and q-lines. On the left of this plaitpoint the q-line lies at larger volumes, on the right on the other hand at smaller volumes than the p-line, the latter changing its course soon after again from one going to the right into one going to the left.

This plaitpoint, however, is not to be realised. With the two plaitpoints discussed above all the p-line and all the q-line, at least in the neighbourhood of that point, lie outside the spinodal curve, and so in the stable region. In this case they lie within the unstable region.

Summarizing what has been said about fig. 8, we see that there is a group of q-lines which cut the spinodal curve in four points. The outside lines of this group pass through plaitpoints. That with the highest value of q passes through the plaitpoint that is to be realised; that with the lowest value of q passes through the plaitpoint that is not to be realised. All the q-lines lying outside this group intersect the spinodal curve only in two points. If, however, the temperature chosen should lie above $(T_k)_2$ the q-lines of still higher degree than of that, passing through the vapour-liquid-plaitpoint, will no longer cut the spinodal curve.

And finally one more remark on the spinodal curve, which may occur in the case of fig. 8. By making the line $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^2\psi}{dx^2}=0$ intersect, we have a region, in which both $\frac{d^2\psi}{dv^2}$ and $\frac{d^2\psi}{dx^2}$ is negative. In such a region the product of these quantities is again positive, and it may become equal to $\left(\frac{d^2\psi}{dxdv}\right)^2$. If this should be the case, it takes again place in a locus which forms a closed curve. Within this region there is then again a portion of the spinodal curve which is quite isolated from the spinodal curve considered. With regard to the p- and q-lines this implies, that there both $\frac{dv}{dx_p}$ and $\frac{dv}{dx_q}$ is negative; and so that contact is not impossible. Such a portion of a spinodal curve encloses then a portion of the ψ-surface which is concave-concave seen from below. If we consider the points lying within the spinodal curve as representing unstable equilibria, the points within this isolated portion of the spinodal curve are a fortiori unstable. The presence of such a portion of a spinodal curve not being conducive to the insight of the states which are liable to realisation, we shall devote no more attention to them.

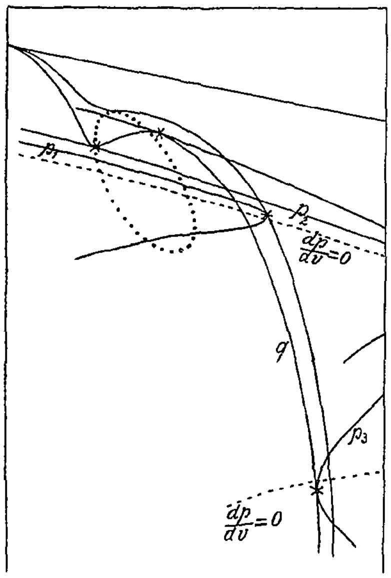

Fig. 8.

It appears from this description and from the drawing (fig. 8) that in this case the spinodal curve has a more complicated course than it would have if the curve $\frac{d^2\psi}{dx^2}=0$ did not exist. It has a portion on the liquid side in which it is forced towards smaller volumes. There is, however, no reason to speak here of a longitudinal plait. We might speak of a more or less complicated plait here. But we shall only use the name of longitudinal plait, when we meet with a portion that is quite detached from the ordinary plait, which portion will then on the whole run in the direction of the v-axis.

There remains an important question to be answered: "What happens to the spinodal curve and to the plaitpoints with increase of temperature?"

At the temperature somewhat higher than $(T_k)_2$ there exist 3 plaitpoints in the diagram. 1. The realisable one on the side of the liquid volumes. 2. The hidden plaitpoint also on the side of the liquid volumes. 3. The realisable vapour-liquid plaitpoint. Let us call them successively P_1, P_2 and P_3. Now there are two possibilities, viz. 1. that with rise of the temperature P_1 and P_2 approach each other and coincide, and the plait has resumed its simple shape before P_3 disappears at $T = (T_k)_1$; and 2. that with rise of T the points P_2 and P_3 coincide and disappear, and also in that case the plait has resumed a simple shape. In the latter case, however, the plaitpoint is to be expected at very small volumes, and so also at very high pressure. Then, too, all heterogeneous equilibria have disappeared at $T = (T_k)_1$. Perhaps there may be still a third possibility, viz. when the locus $\frac{d^2\psi}{dx^2} = 0$ would disappear at a temperature higher than $(T_k)_1$. Besides the plaitpoint P_1 another new plaitpoint would then make its appearance at $T = (T_k)_1$ on the side of the first component. This would transform the plait into an entirely closed one, and only above the temperature, at which $\frac{d^2\psi}{dx^2} = 0$ vanishes, all heterogeneous equilibria would have disappeared.

Let us now briefly discuss these different possibilities. We shall restrict ourselves to the description of what happens in those cases, and at least for the present leave the question unsettled on what properties of the two components it depends whether one thing or another takes place. If P_1 and P_2 coincide, the portion of the locus $\frac{d^2\psi}{dx^2} = 0$ which we have drawn in fig. 8 for smaller volumes than that of $\frac{d^2\psi}{dv^2} = 0$, must have got entirely or almost entirely within the region where $\frac{d^2\psi}{dv^2}$ is negative in consequence of the rise of temperature, or the whole locus $\frac{d^2\psi}{dx^2} = 0$ may have disappeared with rise of T.

Now at P_1 in the previously given equation:

$$dv_p - dv_q = \frac{1}{1.2.3} \left\{ \left(\frac{d^3v}{dx^3}\right)_p - \left(\frac{d^3v}{dx^3}\right)_q \right\} dx^3$$

the factor of dx^3 is negative, but at P_2 this factor is positive. If the points P_1 and P_2 coincide, this factor $= 0$. With coincidence of these plaitpoints, called *heterogeneous* plaitpoints by KORTEWEG, besides $\left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q$ and $\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q$, also $\left(\frac{d^3v}{dx^3}\right)_p = \left(\frac{d^3v}{dx^3}\right)_q$.

If P_2 and P_3 coincide, $\frac{d^2\psi}{dv^2} = 0$ has contracted with rise of temperature. Also $\frac{d^2\psi}{dx^2} = 0$ contracts with rise of the temperature and is displaced as a whole, as I hope to demonstrate further. But the contraction of $\frac{d^2\psi}{dv^2} = 0$, whose top moves to the left, happens relatively quicker, so that e.g. the top falls within the region in which $\frac{d^2\psi}{dx^2}$ is negative. The existence of the point P_3 requires that $\left(\frac{dv}{dx}\right)_q$ is positive. The point P_2 lies on the right of $\frac{d^2\psi}{dx^2} = 0$ and above $\frac{d^2\psi}{dv^2} = 0$. If the top of $\frac{d^2\psi}{dv^2} = 0$ lies within the curve $\frac{d^2\psi}{dx^2} = 0$, neither P_2 nor P_3 can exist any longer. Before this relative position of the two curves they have, therefore, already disappeared in consequence of their coinciding. Also in this case the coincidence of *heterogeneous* plaitpoints holds. At P_2 the factor of dx^3 was positive, and at P_3 this factor is negative. In case of coincidence $\left(\frac{d^3v}{dx^3}\right)_p = \left(\frac{d^3v}{dx^3}\right)_q$. With further rise of T, however, the top of $\frac{d^2\psi}{dv^2} = 0$ will have to get again outside the region where $\frac{d^2\psi}{dx^2}$ is negative. The curve $\frac{d^2\psi}{dx^2} = 0$, namely, cannot extend to $x = 0$, and the curve $\frac{d^2\psi}{dv^2} = 0$ at $T = (T_k)$, has its top at $x = 0$. We draw from this the conclusion, that

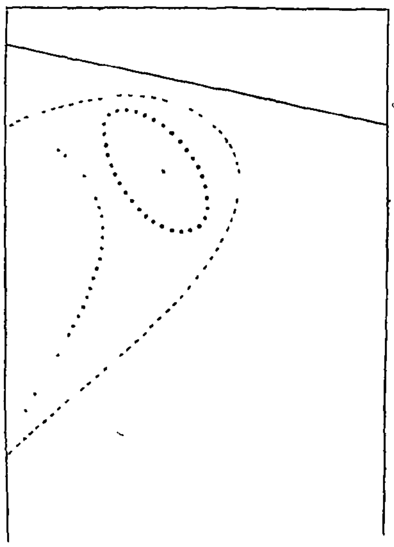

Fig. 9.

with continued increase of temperature the curves $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$ will no longer intersect, but will assume the position indicated by fig. 9.

The spinodal line runs round the two curves, and so in consequence of the presence of $\frac{d^2\psi}{dx^2}=0$ it is forced to remain at an exceedingly large distance from the curve $\frac{d^2\psi}{dv^2}=0$. The question may be raised whether the spinodal curve cannot split up into two separated parts, one part enclosing the curve $\frac{d^2\psi}{dv^2}=0$, the other part passing round $\frac{d^2\psi}{dv^2}=0$. The answer must then be: probably not. In the points between the two curves $\frac{d^2\psi}{dv^2}$ and $\frac{d^2\psi}{dx^2}$ are indeed, positive, but still small, whereas $\frac{d^2\psi}{dx\,dv}$ does not at all occur in the figure, and will, therefore, in general, be large. Now if the temperature at which $\frac{d^2\psi}{dx^2}=0$ disappears, should lie above $(T_k)_1$, $\frac{d^2\psi}{dv^2}=0$ shifts to the left, till it leaves the figure, and the spinodal curve is closed at $x=0$ and $T=(T_k)_1$, and the new plaitpoint makes its appearance, which we mentioned above. From this moment we have a spinodal curve with two realisable plaitpoints. The graphical representation of the curvature of the p- and the q-lines is in this case very difficult, because both groups of lines have only a slight curvature. If, however, we keep to the rule, that the p- and the q-lines envelop the spinodal curve at realisable plaitpoints, we conclude that the value of $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ is positive in P_1, and negative in the other plaitpoint. When these points, called *homogeneous* plaitpoints by KORTEWEG, coincide, $\left(\frac{d^2v}{dx^2}\right)_p=\left(\frac{d^2v}{dx^2}\right)_q=0$. Above the temperature at which this takes place, the p- and the q-lines have no longer any point of contact. In consequence of the disappearance of the locus $\frac{d^2\psi}{dv^2}=0$, the course of the p-lines has become chiefly from left to right, so in the direction of the x-axis. On account of the disappearance of the locus

$\frac{d^2\psi}{dx^2} = 0$ the course of the q-lines has also been simplified, and at least with a volume which is somewhat above the limiting volume, they run chiefly in the direction of the v-axis.

Many of the results obtained about the course of the spinodal curve, and about the place of the plaitpoints, at which we have arrived in the foregoing discussion by examining the way in which the p- and the q-lines may be brought into mutual contact, may be tested by the differential equation of the spinodal line. This will, of course, also be serviceable when we choose another region than that discussed as yet.

From :

$$\frac{d^2\psi}{dv^2}\frac{d^2\psi}{dx^2} - \left(\frac{d^2\psi}{dxdv}\right)^2 = 0.$$

we derive:

$$\left\{\frac{d^2\psi}{dx^2}\frac{d^3\psi}{dv^3} + \frac{d^2\psi}{dv^2}\frac{d^3\psi}{dx^2dv} - 2\frac{d^2\psi}{dxdv}\frac{d^3\psi}{dxdv^2}\right\} dv +$$

$$+ \left\{\frac{d^3\psi}{dx^3}\frac{d^2\psi}{dv^2} + \frac{d^2\psi}{dx^2}\frac{d^3\psi}{dxdv^2} - 2\frac{d^2\psi}{dx^2}\frac{d^3\psi}{dx^2dv}\right\} dx +$$

$$+ \left\{-\frac{d^2\eta}{dx^2}\frac{d^2\psi}{dv^2} - \frac{d^2\eta}{dv^2}\frac{d^2\psi}{dx^2} + 2\frac{d^2\eta}{dxdv}\frac{d^2\psi}{dxdv}\right\} dT = 0.$$

We arrive at the shape of the factor of dT by considering that from:

$$d\varepsilon = T\,d\eta - p\,dv + q\,dx$$

follows :

$$d\psi = -\eta\,dT - p\,dv + q\,dx$$

so that $\left(\frac{d\psi}{dT}\right)_{v,x} = -\eta$ and so $\frac{d^3\psi}{dTdv^2} = -\left(\frac{d^2\eta}{dv^2}\right)_{x,T}$ etc.

This very complicated differential equation may be reduced to a simple shape.

Let us for this purpose first consider the factor of dv. By substituting in it the quantity $\dfrac{\left(\frac{d^2\psi}{dxdv}\right)^2}{\frac{d^2\psi}{dv^2}}$ for $\frac{d^2\psi}{dx^2}$, and $\left(\frac{dv}{dx}\right)_p$ for $-\dfrac{\frac{d^2\psi}{dx\,dv}}{\frac{d^2\psi}{dv^2}}$

this factor becomes :

$$\frac{d^2\psi}{dv^2}\left\{\frac{d^3\psi}{dv^3}\left(\frac{dv}{dx}\right)_p^2 + 2\frac{d^3\psi}{dxdv^2}\left(\frac{dv}{dx}\right)_p + \frac{d^3\psi}{dx^2dv}\right\}.$$

From $p = -\frac{d\psi}{dv}$ we derive :

$$\frac{d^2\psi}{dv^2}\left(\frac{dv}{dx}\right)_p+\frac{d^2\psi}{dxdv}=0$$

and

$$\frac{d^2\psi}{dv^2}\left(\frac{d^2v}{dx^2}\right)_p+\left\{\frac{d^3\psi}{dv^3}\left(\frac{dv}{dx}\right)_p^2+2\frac{d^3\psi}{dv^2dx}\left(\frac{dv}{dx}\right)_p+\frac{d^3\psi}{dx^2dv}\right\}$$

from which appears that we can write the factor of dv in the form of:

$$-\left(\frac{d^2\psi}{dv^2}\right)^2\left(\frac{d^2v}{dx^2}\right)_p.$$

We might proceed in a similar way with regard to the factor of dx, but we can immediately find the shape of this factor by substituting the quantity x for v and q for p in the factor of dv. We find then:

$$-\left(\frac{d^2\psi}{dx^2}\right)^2\left(\frac{d^2x}{dv^2}\right)_q.$$

As long as we keep T constant, and this is necessary for the course of a spinodal curve, the differential equation, therefore, may be written:

$$-\left(\frac{d^2\psi}{dv^2}\right)^2\left(\frac{d^2v}{dx^2}\right)_p dv-\left(\frac{d^2\psi}{dx^2}\right)^2\left(\frac{d^2x}{dv^2}\right)_q dx=0.$$

By taking into account that $\left(\frac{d^2x}{dv^2}\right)_q=-\left(\frac{dx}{dv}\right)_q^3\left(\frac{d^2v}{dx^2}\right)_q$, we obtain after some reductions which do not call for any explanation, the simple equation:

$$\left(\frac{dv}{dx}\right)_{spin}=\left(\frac{dv}{dx}\right)_{p=q}\frac{\left(\frac{d^2v}{dx^2}\right)_q}{\left(\frac{d^2v}{dx^2}\right)_p}.$$

As a first result we derive from this equation the thesis, that $\left(\frac{dv}{dx}\right)_{spin}$ and $\left(\frac{dv}{dx}\right)_{p=q}$ must have the same sign, if $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ have the same sign and vice versa. Thus on the vapour side in fig. 7 $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ have always reversed sign, and $\left(\frac{dv}{dx}\right)_{p=q}$ being negative, $\left(\frac{dv}{dx}\right)_{spin}$ is negative on the vapour branch of the spinodal curve. Reversely the curvatures of the p and q-lines have the same sign on the liquid side, and $\left(\frac{dv}{dx}\right)_{bin}=\left(\frac{dv}{dx}\right)_{p=q}=$ positive. If, however,

$\left(\frac{d^2v}{dx^2}\right)_q$ should have been indeed negative there, as was accidentally represented in point 2 of the spinodal curve, the spinodal curve runs towards smaller volumes with increasing value of x. So if there occur points with maximum or minimum volume on the spinodal curve, $\left(\frac{d^2v}{dx^2}\right)_q = 0$ in those points. If on the other hand $\left(\frac{dv}{dx}\right)_{spin}$ is infinitely large, which occurs in the case under consideration when the spinodal curve is closed on the right side for $T > (T_k)_2$ then $\left(\frac{d^2v}{dx^2}\right)_p$ must be $= 0$, and so the p-line must have a point of inflection in such a point, to which we had moreover already concluded before in another way. A great number of other results may be derived from this differential equation of the spinodal line. We shall, however, only call attention to what follows. In a plaitpoint $\left(\frac{dv}{dx}\right)_{spin} = \left(\frac{dv}{dx}\right)_{p=q}$. For a plaitpoint it follows from this that $\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q$.

If for a point of a spinodal curve $\left(\frac{dv}{dx}\right)_{spin}$ is indefinite, both $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ must be equal to 0. This takes place in two cases: 1. in a case discussed above when the whole of the spinodal line is reduced to one single point. 2. when a spinodal line splits up into two branches, as is the case for mixtures for which also T_k minimum is found. In the former case the disappearing point has the properties of an isolated point, in the second case of a double point.

In the differential equation of the spinodal line the factor of dT may be written:

$$-\frac{1}{T}\left\{\left(\frac{d^2T\eta}{dx^2}\right)_{vT}\frac{d^2\psi}{dv^2} - 2\left(\frac{d^2T\eta}{dxdv}\right)_T\frac{d^2\psi}{dxdv} + \left(\frac{d^2T\eta}{dv^2}\right)_{Tx}\frac{d^2\psi}{dx^2}\right\}$$

and by putting $\varepsilon - \psi$ for $T\eta$ it may be reduced to:

$$-\frac{1}{T}\left\{\frac{d^2\psi}{dv^2}\frac{d^2\varepsilon}{dx^2} - 2\frac{d^2\psi}{dxdv}\frac{d^2\varepsilon}{dxdv} + \frac{d^2\psi}{dx^2}\frac{d^2\varepsilon}{dv^2}\right\}$$

or to

$$-\frac{1}{T}\frac{d^2\psi}{dv^2}\left\{\frac{d^2\varepsilon}{dv^2}\left(\frac{dv}{dx}\right)_{p=q}^2 + \frac{d^2\varepsilon}{dxdv}\left(\frac{dv}{dx}\right)_{p=q} + \frac{d^2\varepsilon}{dx^2}\right\}.$$

The factor by which $-\frac{1}{T}\frac{d^2\psi}{dv^2}$ is to be multiplied, occurs for the first time in formula (4) Verslag K. A. v. W. Mei 1895, and at the close of that communication I have written this factor in the form:

$$-\frac{2a}{v}\left\{\left(\frac{1}{v}\frac{dv}{dx_v}-\frac{1}{2a}\frac{da}{dx}\right)^2+\frac{a_1a_2-a_{12}^2}{a^2}\right\},$$

from which appears that in any case when $a_1a_2 > a_{12}^2$, this factor is negative. Here, too, I shall assume this factor to be always negative, but I may give a fuller discussion later on.

In consequence of these reductions the differential equation of the spinodal curve may be written as follows:

$$\frac{d^2\psi}{dv^2}\left(\frac{d^2v}{dx^2}\right)_{pT}dv+\frac{d^2\psi}{dxdv}\left(\frac{d^2v}{dx^2}\right)_{qT}dx+\frac{dT}{T}\left(-\right)=0.$$

From this equation follows inter alia this rule concerning the displacement of the spinodal curve with increase of T, that on the side where $\left(\frac{d^2v}{dx^2}\right)_p$ is positive, the value of v with constant value of x, increases, and the reverse. So the two branches of a spinodal curve approach each other with increase of the temperature. But I shall not enter into a discussion of the further particulars which might occur when this formula is applied. By elimination of dv I shall only derive the differential equation of the spinodal line when we think it given by a relation between p, x and T. We find then:

$$\left(\frac{d^2v}{dx^2}\right)dp=\left(\frac{dp}{dx}\right)_{v,T}\left[\left(\frac{d^2v}{dx^2}\right)_{p,T}-\left(\frac{d^2v}{dx^2}\right)_{q,T}\right]dx+\frac{dT}{T}\left[(-)+T\left(\frac{dT}{dp}\right)_{v,x}\left(\frac{d^2v}{dx^2}\right)_{pT}\right]$$

for a plaitpoint the factor of dx disappears, and we find back the equation (4). Verslag K. A. v. W. Mei 1895, for the plaitpoint curve. At constant temperature we find for the spinodal curve:

$$\left(\frac{dp}{dx}\right)_{spin}=\left(\frac{dp}{dx}\right)_v\left\{1-\frac{\left(\frac{d^2v}{dx^2}\right)_q}{\left(\frac{d^2v}{dx^2}\right)_p}\right\}.$$

(*To be continued*).

51*