Citation:

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osculating plane of C_1 in R. Through R and five points of C_1 consecutive to R a twisted cubic C^3 can be brought, on the condition that R, l and V are an ordinary point, an ordinary tangent and an ordinary osculating plane of C_1. The developable D^1 formed by the tangents to C^3 and the developable D_1 have in common the line l and four consecutive generating lines.

If l must count for 2, 3 or 4 common tangents of C^3 and S, this is also the case for C_1 and S. The theorems proved in § 6 and 7 for C^3 hold good for any twisted curve. This gives rise to the following theorems:

If the developable D_1 corresponding to curve C_1 touches any surface S in point P whilst the generating line l of D_1 through P is no inflexional tangent of S, the line l counts for two or for three common tangents to C_1 and S according to the surfaces having in P an ordinary or a stationary contact.

If the point of contact P of D_1 and S be a parabolic point on S, then l counts for four or for two common tangents of C_1 and S according as the inflexional tangent of S in P coinciding with l or not.

If the point of contact P of D_1 and S be a hyperbolic point on S and if the tangent l of C_1 coincides with an inflexional tangent in the point P of S, then l counts for four or for two common tangents of C_1 and O according to R coinciding with P or not.

If C_1 touches S in P, whilst the osculating plane of C_1 in P coincides with the tangent plane of S in P, then the tangent l in P to C_1 counts for four or for three common tangents of C_1 and O, according to l being an inflexional tangent of O in P or not.

The theorems proved here for curves in space hold with a slight modification (see § 1) still for plane curves. They can be easily proved by taking for C_1 first a parabola p^2 after which they can be directly extended to an arbitrary conic section and after this to an arbitrary plane curve.

Delft, June 1905.

Physics. — *The shape of the sections of the surface of saturation normal to the x-axis, in case of a three phase pressure between two temperatures."* By Prof. J. D. VAN DER WAALS.

In these Proceedings of March 1905 I have (fig. 4, 5 and 6) represented in a diagram some sections of the (p, T, x)-surface normal to the T-axis for three temperatures, at which three phases can exist simultaneously. The three temperatures chosen were: 1^{st} the temperature which we might call the transformation temperature and which I shall indicate by T_{tr} (fig. 5), 2nd a temperature a little below the transformation temperature (fig. 4) and 3rd one a little above T_{tr}.

In the case that these sections are known for all possible temperatures, the saturation surface is of course quite determined and known, and so all other sections e.g. those normal to the x-axis, are also determined. But it appears from the given figures, that though the realizable part of the saturation surface has a comparatively simple shape, the non-realizable part has a fairly intricate course — and that it is necessary to know also that intricate portion if we wish to get an insight into the course of the part that is to be realized.

To the intricacy of the hidden part it is due that though all the sections normal to the x-axis are given by those normal to the T-axis, the shape of the $(p, T)_x$-sections will not always be easy to derive. Now that I for myself have obtained an insight into the course of these sections I have thought it not devoid of interest to try and make clear the properties of this curve by means of a series of successive figures.

If we wish to represent these $(p, T)_x$ figures in a diagram, all the surface must of course be known — in other words according to the course of our derivation from the $(p, x)_T$ sections — *all* the $(p, x)_T$ sections must be known.

Between two temperatures which are known by experiment, see fig. 4, 5 and 6 l.c., such a $(p, x)_T$ section has two tops, viz. P and Q. If T is raised, the part that has P as top, is narrowed, and the part that has Q as top widens, and the reverse. This property is perhaps not quite fulfilled in the schematical figures of the paper mentioned, but it follows immediately from the fact that with continued rise of temperature the top P vanishes, whereas with sufficient lowering of T the top Q vanishes. Let us call the temperature at which P vanishes T_e and that at which Q disappears T_a. I choose these symbols T_e and T_a, because I think of the mixture of ethane and alcohol as an example for the shape of the (p, T, x)-surface discussed here. Of these mixture the plaitpoint circumstances have been determined by KUENEN and ROBSON. At T_e the whole top the plaitpoint of which is P, will have contracted, and the only trace left on the outline of the (p, x)-figure of the complication found at lower values of T, is a point, at which the tangent is horizontal, while at that place there must be an inflection point in the (p, x)-curve, which has for the rest a continuous course. For T equal to T_a this is the case for the point Q vanishing on the outline. Just as experiment yields the values of T_e and T_a, it also gives us the values of x_e and x_a at which the tops P and Q will disappear. For temperatures higher than T_e and lower than T_a the $(p, x)_T$-curves have lost the complications which they had for values of T between T_e and T_a. Only at temperatures which lie little above T_e or little below T_a, there is still a deviation to be found from the well-known looplike shape of these figures, as there are inflection points to be found. So at T_e and T_a the complications which I shall call externally visible complications, have disappeared. But before we can say we know all the particularities of the whole (p, T, x)-surface, among which I also reckon the *hidden* complications, the question is to be settled whether the disappearance of the external complications involves the disappearance of the hidden complications, whether perhaps the hidden complications may continue to exist long after the external complications have disappeared. Figures (1) and (2) make clear between which two alternatives a choice must be made. According to fig. (1) the disappearance of the external complications would involve the disappearance of the hidden ones. According to fig. (2) the hidden ones continue to exist when the external ones have disappeared. And even when T rises above T_e, they are still there. At higher values of T the hidden complication gets detached from the outline. The spinodal curve ——— retains its maximum and minimum, and there are still two plaitpoints, viz. at this maximum and minimum. And only at a certain value of T lying above T_e that maximum and minimum have coincided to a double point and the hidden complication is about to disappear.

For the point Q a similar question occurs. Have all the complications disappeared at T_a, or is it required that T descends below T_a before the hidden complications have also disappeared on this side?

I must own that I have long been in doubt on this point, as will appear when we compare the answer I shall now give to this question with remarks I made previously on the experiments of KUENEN and ROBSON.

According to KORTEWEG's result a double plaitpoint will always originate on the spinodal curve. But in itself this does not seem decisive. For according to both figures, to fig. 1 as well as to fig. 2, a double plaitpoint disappears or appears on an existing spinodal curve. But in fig. 1 this takes also place on an existing binodal curve. And now it is KORTEWEG's opinion, that such an appearance of a double point, viz. on an existing binodal curve, would be such a special case that we must not conclude to it but in the utmost

J. D. VAN DER WAALS. The shape of the sections of the surface of saturation normal to the x-axis, in case of a three phase pressure between two temperatures.

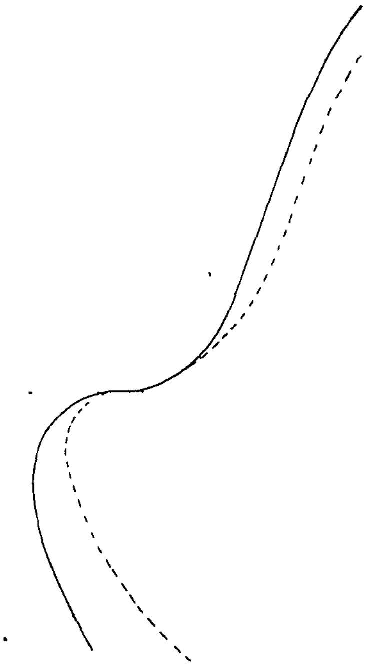

Fig. 1.

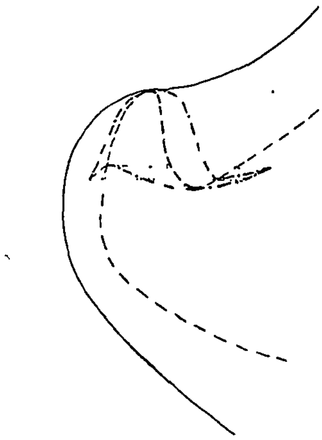

Fig. 2

J. D. VAN DER WAALS. The shape of the sections of the surface of saturation normal to the x-axis, in case of a three phase pressure between two temperatures.

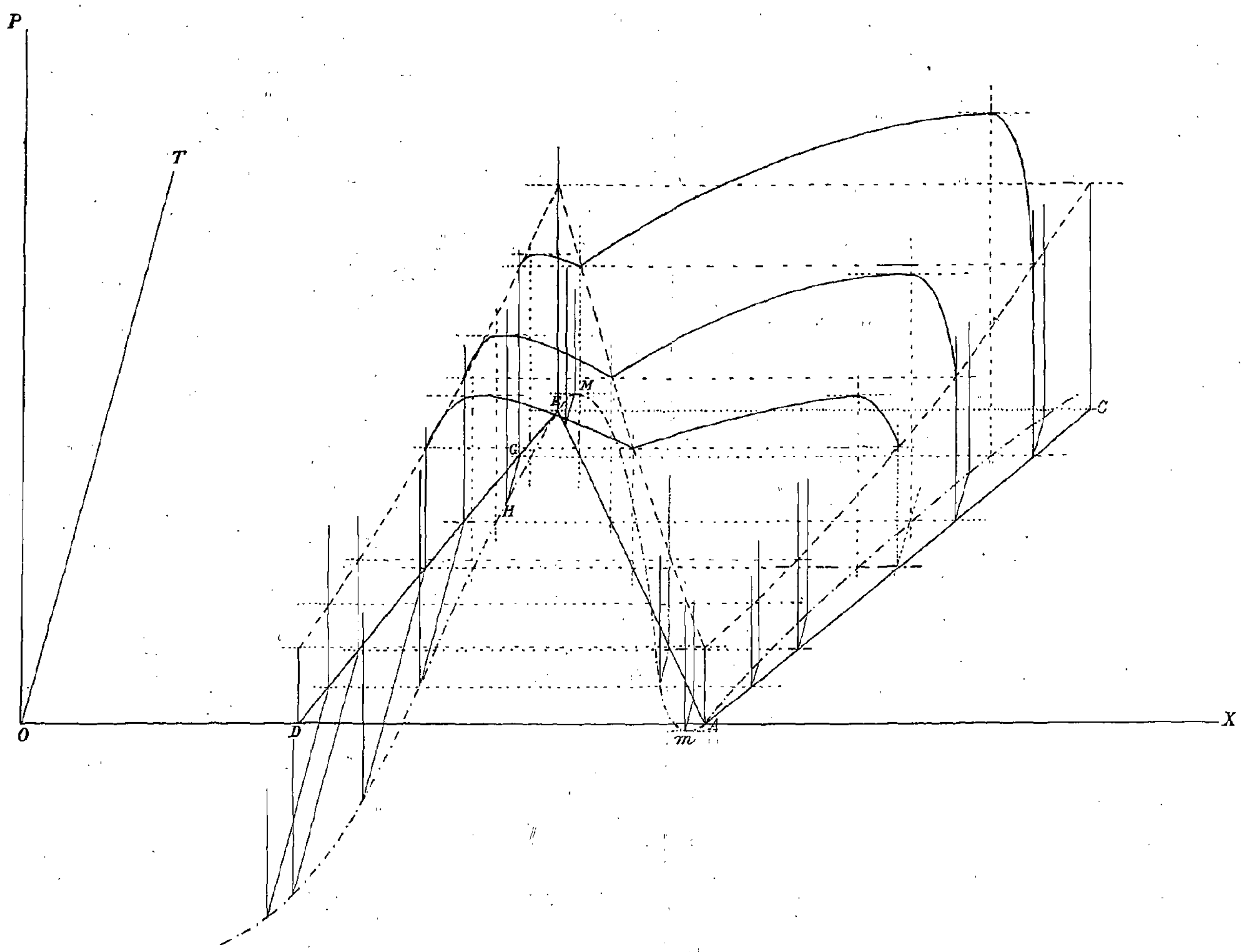

Fig. 3.

J. D. VAN DER WAALS. The shape of the sections of the surface of saturation normal to the x-axis, in case of a three phase pressure between two temperatures.

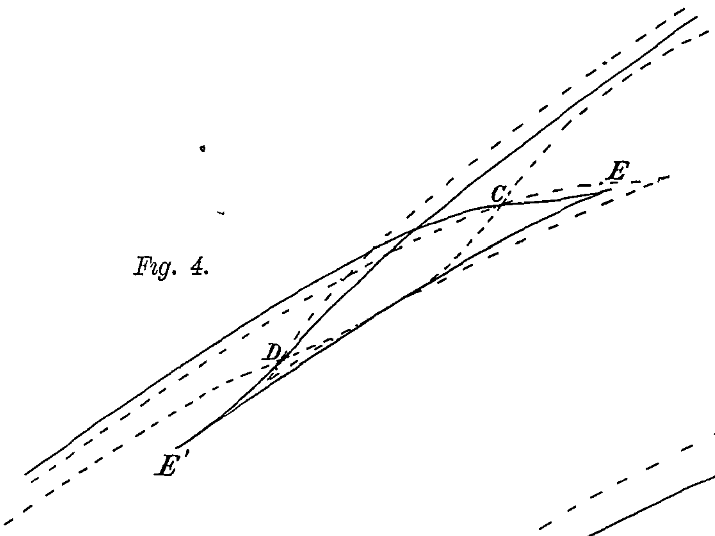

Fig. 4.

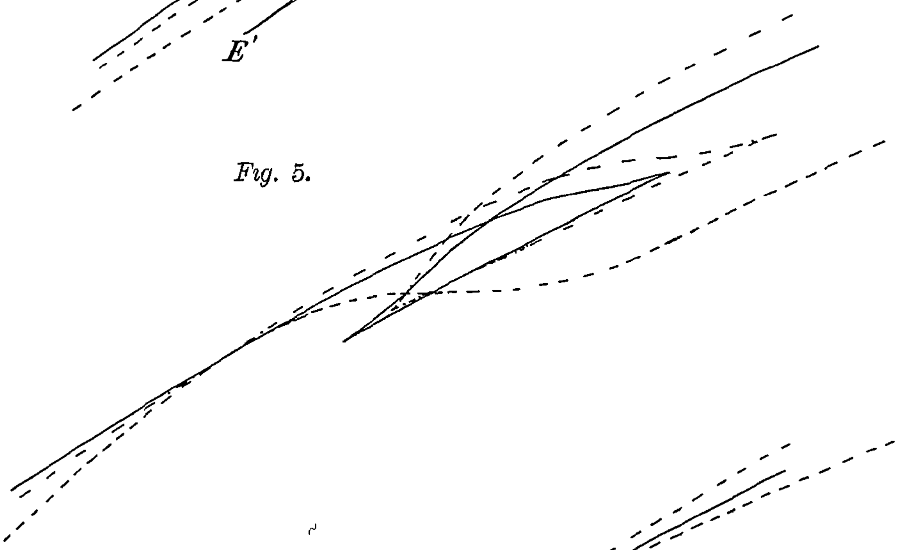

Fig. 5.

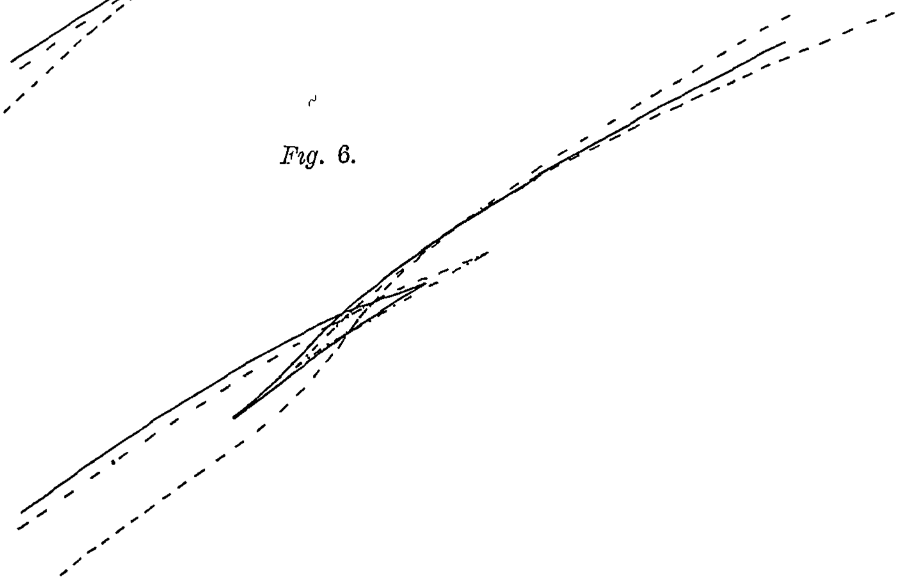

Fig. 6.

J. D. VAN DER WAALS. **The shape of the sections of the surface of saturation normal to the x-axis, in case of a three phase pressure between two temperatures.**

Fig. 7

necessity. This is in fact an argument that speaks for fig. 2, but which did not seem to me perfectly conclusive. For who warrants us, that these very special circumstances do not occur here? It is chiefly to decide this point, that I have also examined the course of the $(p,T)_x$-lines. And this examination has taught me, that the particularities which occur in these lines, do not clash with the assumption which leads to fig. 2 — whereas we should be confronted with difficulties, when we concluded to fig. 1.

Then fig. 3 is drawn up on the supposition that there are still hidden complications beyond the values of T_e and T_a. In this figure is drawn in the first place the projection on the (T, x)-plane of the phases coexisting at the three phase pressure, viz. the continuous curve $DEAC$. So this line represents the locus for the points $A'AA''$ of the figs. 4, 5, 6 of the paper of March 1905. The value of T for the point E is therefore T_e, and for the point A, T has the value of T_a. That this broken line consists of three almost straight pieces is not essential, but it *has* been assumed that it does not change its direction continuously at the points E and A.

In the second place the projection of the plaitpoint line has been given by: —— . ——. It consists of a piece which may be considered as the projection of the points P of the figures of March 1905, i.e. the left part up to the point E. The part lying on the right from the point A represents then the projection of the points Q of the figures l. c. Every part of this line lying between E and A is projection of the hidden plaitpoints.

As we make one double plaitpoint disappear at $T > T_e$, and the other at $T < T_a$, this middle part starts on the left still running to higher values of T, (the piece EM) and on the right there is a piece mA, that also runs to higher values of T. The remaining part of this plaitpoint projection curve, viz. the piece Mm descends therefore with increasing value of x. That this plaitpoint curve possesses a maximum and a minimum value will be shown presently. This middle piece is the locus of the plaitpoints R of the figs. 4, 5, 6 l. c. The part between E and M, and also the part between A and m is the projection of the higher plaitpoint of the hidden complication in the cases that this complication still exists either above T_e or below T_a.

In the third place the three phase pressure is traced. In the points of the line DE thinner lines have been drawn parallel to the p-axis, increasing in length as we reach the point E. The three phase pressure itself is denoted by — — — —. We must, of course, take care that points of the branch of the three phase pressure lying above EA, and also of the branch lying above AC must fulfil the condition that for the same value of T the pressure must have the same value for the three branches.

In the fourth place for some values of T sections parallel to the (p,x)-plane are given and those parts of these sections are drawn which correspond to the pieces $A'PA$ and AQA'' of the figs. 4, 5, 6 l. c. We must then, of course, take care that the maxima of the curves fall above the projection of the plaitpoint curve. It is hardly necessary to remark that at any rate as long as T lies between T_e and T_a the plaitpoint pressure for the left-hand branch, and also for the right-hand branch is greater than the three phase pressure. But if we want to compare the value of the plaitpoint pressure and that of the three phase pressure *at the same value of x*, we have to carry out another construction. Let G be a point of the projection of the three phase pressure. Let us draw the line GH parallel to the T-axis, then H (a point of the projection of the plaitpoint curve) has the same value of x, and so above H a point must be sought of the plaitpoint curve itself. How high this point lies depends on the value which the plaitpoint pressure has for this value of x. In the point H a somewhat thicker line has been drawn parallel to the p-axis, whose length would have to denote the value of this plaitpoint pressure. This length is left undetermined in the figure — but is clear that it will be smaller than the amount of the three phase pressure for the same value of x. For at the value of T, as it is for the point G, the pressure above G in the section for the chosen value of x is equal to the three phase pressure. The value of T for the point H is smaller than that for G. Between these two values of T the $(p,T)_x$-section of the (p,T,x)-surface has a continuous course, and in such a $(p,T)_x$-curve the pressure rises with the temperature. Only in the case that a maximum in the $(p,x)T$-curve occurred, the pressure above H, so the plaitpoint pressure could be smaller than that above G. But in our diagrams we shall assume the more general case. Themodifications which would ensue from the assumption that in the region discussed here a maximum pressure occurs, would render numerous new figures necessary, and it will not be difficult to give them when the more common case has been understood.

According to fig. 3 there is in our case a maximum and a minimum for T_{pl}, so that there are values of x for which $\frac{dT_{pl}}{dx} = 0$. For a plaitpoint $\left(\frac{d^2\zeta}{dx^2}\right)_{pT}$ is equal to 0, because it is a point of the spinodal curve, and at the same time $\left(\frac{d^3\zeta}{dx^3}\right)_{pT}$ is equal to 0.

The differential equation of the spinodal curve is

$$\left(\frac{d^3\zeta}{dx^3}\right)_{pT} dx + \left(\frac{d^2 v}{dx^2}\right)_{pT} dp - \left(\frac{d^2\eta}{dx^2}\right)_{pT} dT = 0. \quad . \quad . \quad . \quad (1)$$

The differential equation of the plaitpoint curve is

$$\left(\frac{d^4\zeta}{dx^4}\right)_{pT} dx + \left(\frac{d^3 v}{dx^3}\right)_{pT} dp - \left(\frac{d^3\eta}{dx^3}\right)_{pT} dT = 0. \quad . \quad . \quad . \quad (2)$$

From (1) follows:

$$\left(\frac{dp}{dT}\right)_{Spin} = \frac{\left(\frac{d^2\eta}{dx_2}\right)_{pT}}{\left(\frac{d^2 V}{dx^2}\right)_{pT}}$$

If we substitute this value of $\frac{dp}{dT}$ in (2), we find:

$$\left(\frac{dT}{dx}\right)_{pl} = -\frac{\left(\frac{d^2 v}{dx^2}\right)_{pT}\left(\frac{d^4\zeta}{dx^4}\right)_{pT}}{\left(\frac{d^3 v}{dx^3}\right)_{pT}\left(\frac{d^2\eta}{dx^2}\right)_{pT} - \left(\frac{d^2 v}{dx^2}\right)_{pT}\left(\frac{d^3\eta}{dx^3}\right)_{pT}} \quad . \quad . \quad . \quad . \quad (3)$$

and

$$\left(\frac{dp}{dx}\right)_{pl} = -\frac{\left(\frac{d^2\eta}{dx^2}\right)_{pT}\left(\frac{d^4\zeta}{dx^4}\right)_{pT}}{\left(\frac{d^3 v}{dx^3}\right)_{pT}\left(\frac{d^2\eta}{dx^2}\right)_{pT} - \left(\frac{d^2 v}{dx^2}\right)_{pT}\left(\frac{d^3\eta}{dx^3}\right)_{pT}} \quad . \quad . \quad . \quad . \quad (4)$$

From this equation (3) follows that $\left(\frac{dT}{dx}\right)_{pl}$ can become 0 when $\left(\frac{d^2v}{dx^2}\right)_{pT} = 0$. In this case $\left(\frac{dp}{dx}\right)_{pl}$ is not equal to 0. A similar case is found for substances, for which no three phase pressure occurs when there exists a minimum critical temperature. It is wellknown that in this case the binodal curve splits up, and that there is a point of inflection for the isopiest in this point. There is a double plaitpoint also then, which originates or disappears at a certain temperature; but though we can speak of a double plaitpoint, the value of $\left(\frac{d^4\zeta}{dx^4}\right)_{pT}$ is not $= 0$ then.

In the case under consideration the value of $\left(\frac{d^4\zeta}{dx^4}\right)_{pT}$ *is* equal to 0 in the point at which a double plaitpoint appears or disap-

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pears, as may be derived from the figs. 1, 2, 3, l. c. Between certain values of p and at suitable values of T there are isopiests, on which $\frac{d^2\zeta}{dx^2}_{pT}$ is four times equal to 0. On such isopiests $\frac{d^3\zeta}{dx^3}_{pT}$ is three times and $\frac{d^4\zeta}{dx^4}_{pT}$ twice equal to 0. We now can choose the value of p and T such, that these two points in which $\frac{d^4\zeta}{dx^4}_{pT}$ is 0, coincide. As then two values of x in which $\frac{d^2\zeta}{dx^2}_{pT}=0$ also coincide, such a point is a plaitpoint. For such points $\left(\frac{d^2\zeta}{dx^2}\right)_{pT}$ and $\left(\frac{d^3\zeta}{dx^3}\right)_{pT}$ and $\left(\frac{d^4\zeta}{dx^4}\right)_{pT}$ is equal to 0. These three equations determine then the value of x, p and T, at which such a double plaitpoint appears or disappears.

If in (3) and (4) we put the quantity $\left(\frac{d^4\zeta}{dx^4}\right)_{pT}=0$, then both $\left(\frac{dT}{dx}\right)_{pl}$ and $\left(\frac{dp}{dx}\right)_{pl}$ will also be equal to 0, from which follows that not only the plaitpoint temperature, but also the plaitpoint pressure will present a maximum and a minimum. As we only assume the case that $\frac{dp}{dT}$ is positive, there will be found at the same time a maximum value or a minimum value for the two curves. In the points E and A there is therefore no maximum or minimum for the plaitpoint curves, and this is also to be expected for the curve of the three phase temperature, though this perhaps might call for further examination. For the properties which are to be derived by us this is, however, not of great importance.

Let us now proceed to describe the properties of the sections of the (p, T, x)-surface normal to the x-axis or in other words the course of the $(p, T)_x$-curves.

We remark then in the first place that for values of x below x_D and above x_C the $(p, T)_x$-curves will present their usual shape without any complication. For values of x between x_D and x_E and also for values of x between x_A and x_C there is a complication in these $(p, T)_x$-lines. For values of x between x_D and x_E the three phase temperature lies higher than the plaitpoint temperature; the reverse is the case for x between x_A and x_C. On such $(p, T)_x$-curves the usual plaitpoint occurs, but at a plaitpoint such curves, considered in themselves, do not present any particularity. But a point also occurs on them at which the three phase pressure is reached, and at such a point the curve suffers an abrupt change of direction. As for every value of x the line $DEAC$ is met only once, this sudden change of direction occurs only once in a $(p, T)_x$-curve. This determines the external course of such a section sufficiently. Beyond the point of change of direction the points for which W_{21} and V_{21} are equal to 0 will give rise to a maximum value and to a critical point of contact. But we confine ourselves here to the modifications which are the consequence of the three phase equilibria.

In the points, at which such an abrupt change of direction occurs, a part of the internal or hidden course of such a $(p, T)_x$-curve begins and the series of figures (a, b, c, d etc.) indicates this hidden course for the values of x, for which the three phase curve is met. Seen on the $(p, T)_x$-curve such a point presents itself as a node. The part of the curve coming from below continues through the node, also the part coming from above, while there is a third part which joins the points, where this onward course stops. The temperature of the node is, therefore, quite determined by the point at which $DEAC$ is cut by a line parallel to the T-axis with the given value of x as abscis. But the size of the hidden part is very different. As it has quite disappeared beyond x_D and x_C, it is but small for values of x only little greater than x_D or only little smaller than x_C. But chiefly the different hidden parts are distinguished by the occurrence or non-occurrence of a plait-point and when it occurs by the place where it occurs.

In what precedes it has already been remarked that the plaitpoint does not lie hidden for values of x beyond x_E and x_A. But for all values of x between x_E and x_A it lies on the hidden part, so on that which might be called the loop when the $(p, T)_x$-curve is drawn. This appears at once when the $(p, x)_T$-figures are consulted l.c. But depending upon the value of x the plaitpoint can have three different places. It may either lie on that part of the loop which may be considered as the continuation of the lower part of the $(p, T)_x$-curve — or it may lie on the branch of the loop joining the points at which the onward course from below and above stops — or it may lie on the part which may be considered as the continuation of the part coming from above.

The first case occurs for x between x_E and x_M, the second when x lies between x_M and x_m and the third case when x lies between x_m and x_A. So if we have drawn a $(p, T)_x$-curve, e.g. one of the figures of the series (a, b, c, d etc.), and when we proceed in the same direction in such a part, also following the loop, we follow the motion which the plaitpoint has when x changes continuously.

A plaitpoint always being a point where the stable and unstable region meet, it would be incorrect to speak of stable, metastable and unstable plaitpoints. But when we pay attention to the coexisting phases in the neighbourhood of the plaitpoint, the preceding names are appropriate for such phases according to the described situation of the plaitpoints. As long as the plaitpoint lies on the external part of the (p, T, x)-surface, the coexisting phases in its neighbourhood are stable; as long as it lies on those parts of the loop which may be considered as a continuation of the external branches, the coexisting phases in its neighbourhood are metastable, and when the plaitpoint lies on the remaining part of the loop, the coexisting phases in its neighbourhood are unstable.

In the series of the figures $(a, b, c, d$ etc.) is, besides the loop of the $(p, T)_x$-curve and the place of the plaitpoint, also the shape of the spinodal curve indicated. This spinodal curve is the section of the spinodal surface with the plane which has the chosen value of x. All the points of the loop which lie below the spinodal curve represent unstable phases and those which lie above it, metastable or stable ones. Thus e. g. in fig. 4, in which the plaitpoint lies on the retrograde branch of the loop, the spinodal curve is a curve which cuts the loop in two more points. In concordance with the figures 4, 5, 6 l. c. are the points of intersection indicated by the letters D and C. By raising the temperature in these figures, the point C is moved to the left, and when the temperature is lowered, D moves to the right, which makes it possible for them to come into the chosen x-plane.

If from a $(p, T)_x$-curve for a chosen value of x the curve is derived which belongs to a value of $x + dx$, the value of $\left(\frac{dp}{dx}\right)_T$ must be known for every value of T.

If $\left(\frac{dp}{dx}\right)$ is $= 0$, the $(p, T)_x$-curve for the values x and $x + dx$, must have the same value for p. If we draw both the $(p, T)_x$-curve and the curve $(pT)_{x+dx}$ as has been done in the figures 4, 5 and 6, there will be intersection of these two (p, T)-curves in all the points in which $\left(\frac{dp}{dx}\right)_T = 0$. In the figures mentioned the curve for $x + dx$ is represented by —.—., and now the two (p, T)-curves will cut everywhere where the spinodal curve cuts the first (p, T)-curve, according to the property that for coexisting phases $\left(\frac{dp}{dx}\right)_T = 0$ when $\left(\frac{d^2\zeta}{dx^2}\right)_{pT} = 0$. Also in the point where the spinodal curve touches the curve $(p, T)_x$, so in the plaitpoint, such an intersection of the two following $(p, T)_x$-curves takes place. This may be assumed as already known from the properties of a $(p,T)_x$-curve, when there are no complications by hidden equilibria. It might possibly be expected that in a plaitpoint, where besides $\left(\frac{d^2\zeta}{dx^2}\right)_{pT}$, also $\left(\frac{d^3\zeta}{dx^3}\right)_{pT}$ is equal to 0, double intersection and so contact would take place. If, however, we develop the equation which teaches us the value of $\left(\frac{dp}{dx}\right)_T$ viz.

$$v_{21}\left(\frac{dp}{dx_1}\right)_T = (x_2 - x_1)\left(\frac{d^2\zeta}{dx_1^{\,2}}\right)_{pT}$$

for the case of a plaitpoint in the form:

$$\left(\frac{d^2v_1}{dx_1^{\,2}}\right)_{pT}\frac{(x_2-x_1)^2}{2}\left(\frac{dp}{dx_1}\right)_T = (x_2-x_1)\left\{\frac{(x_2-x_1)^2}{2}\left(\frac{d^4\zeta}{dx_1^{\,4}}\right)_{pT}\right\}$$

or

$$\left(\frac{dp}{dx_1}\right)_T = (x_2-x_1)\frac{\left(\frac{d^4\zeta}{dx_1^{\,4}}\right)_{pT}}{\left(\frac{d^2v_1}{dx_1^{\,2}}\right)_{pT}}$$

it appears that in the case of a plaitpoint, the quantity $\left(\frac{dp}{dx}\right)_T$ is only once equal to 0 on account of the factor $x_2 - x_1$.

It may be remarked here for the better understanding of the series of figures (a, b, c etc.) that the first set of four viz. a to d holds for values of x lying between a point halfway x_E and x_A and the point E itself, x moving to continually smaller values. Fig. d holds for x_E. The second set of four values holds for x between x_E and x_D, and Fig. g is the representation for $T = T_t$.

The remaining figures (b', c' etc.) hold for values of x lying on the right side. Fig. g' is the representation for $T = T_t$ on the right side and fig. d' holds for $x = x_A$.

Physics. — *"The (T,x)-equilibria of solid and fluid phases for variable values of the pressure"*, by Prof. J. D. VAN DER WAALS.

In two communications (October and November 1903) I discussed and represented in diagrams for the case of equilibrium between a solid and a fluid phase 1st the (p, x)-figures for constant value of T and 2nd the (p, T)-figures for constant value of x. So only the