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KNAW, Proceedings, 11, 1908-1909, Amsterdam, 1909, pp. 799-812

Physics. — *"On the course of the isobars for binary systems II."* By Prof. PH. KOHNSTAMM. (Communicated by Prof. J. D. VAN DER WAALS).

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

8. The point $x = x_0$, $v = 0$, the signification of which for the course of the lines $\frac{dp}{dv} = 0$ and $\frac{dp}{dx} = 0$ we set forth in the preceding paper (These Proc. 599), is also an exceptional point for the isobars themselves. If we approach this point along the line $x = x_0$, coming from large volumes, the pressure is first zero, ascends then to a maximum, at least for positive a, after which it passes again through zero, and continues to descend to $-\infty$, as appears easily from the formula $\frac{MRT}{v} - \frac{a}{v^2}$. If, on the other hand, we arrive at the point $x = x_0$, $v = 0$ along the line $v = b$, we find for the pressure the value $+\infty$. Also all the intermediate isobars pass through this point, as appears when we substitute $b = \frac{db}{dx} x + \frac{1}{2} \frac{d^2b}{dx^2} x^2$ and $v = \left(\frac{dv}{dx}\right)_p x + \frac{1}{2} \left(\frac{d^2v}{dx^2}\right)_p x^2$ in the equation for the isobar, so assuming the point $x = x_0$, $v = 0$ as origin of coordinates. If further we put $\left(\frac{dv}{dx}\right)_p = \frac{db}{dx}$, we get, disregarding the higher powers:

$$p = \frac{1}{x^2} \left\{ \frac{2\,MRT}{\frac{d^2v}{dx^2} - \frac{d^2b}{dx^2}} - \frac{a}{\left(\frac{db}{dx}\right)^2} \right\}$$

and so, however small x be taken, we can find a point for every value of p satisfying the equation. When a is positive the condition for this is that $\frac{db}{dx} = \frac{dv}{dx}$, so that the isobar touches $v = b$, and further $\frac{d^2v}{dx^2} > \frac{d^2b}{dx^2}$, so the isobar has a smaller radius of curvature than $v = b$, and so has greater volume with equal x.

9. What was said in 7 and 5 enables us to indicate the course of the isobars in the neighbourhood of $x = x_0$, $v = 0$. Coming from the said point and touching there $v = b$ (and so also $\frac{dp}{dv} = 0$) an isobar for a high negative value of p will soon intersect the line

$\frac{dp}{dv}=0$. For as was proved in 5, $\frac{dp}{dv}=0$ lies here at smaller volumes than $\frac{dp}{dx}=0$, and so in the region where $\frac{dp}{dx}$ is positive. The line $\frac{dp}{dx}=0$ gives the minimum value of the pressure for every definite x, and so this minimum value becomes constantly higher towards the right, or in other words an isobar of a certain negative value of p cannot penetrate further to the right than that x, for which this value is reached on $\frac{dp}{dv}=0$. At the intersection with $\frac{dp}{dx}=0$ the isobar is // the x-axis, and afterwards it reaches the line $x=x_0$. The course outside this quadrant has no physical significance. So we get a course as fig. 10 presents for an isobar very close to $x=x_0$.

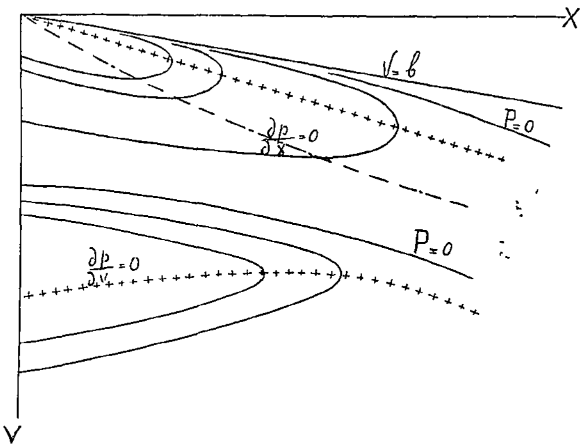

Fig. 10.

But not all the isobars originating from $x=x_0$, $v=0$ will present this course. The question, however, what the shape of the others is, and where the limit lies between the different kinds, can only be discussed when we have gained a complete survey of the points of intersection of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$, also of those lying at a great distance.

10. The results obtained up to now are pretty well independent of the question whether b is a linear, or a quadratic function of x, but now we must distinguish between these two suppositions. For it is clear that for points lying considerably to the right many

quantities will get an entirely different value depending on whether b increases with x or with x^2. Thus the critical temperature becomes infinite in the first case, in the second it approaches a finite amount, the critical pressure becomes finite in the first case, zero in the second, and also the situation of $\frac{dp}{dv}=0$ with respect to $\frac{dp}{dx}=0$ is quite different in one case from that in the other. For if we substitute in the equation:

$$F(v) = -\frac{dp}{dv} = \frac{MRT}{(v-b)^2} - \frac{2a}{v^3}$$

the value of $v-b$, as it holds for $\frac{dp}{dx}=0$, we get:

$$F(v) = \frac{\frac{da}{dx}}{v^2\frac{db}{dx}} - \frac{2a}{v^2}$$

Now we may put $a_1 x^2$ for a for very great value of x, $2a_1x$ for $\frac{da}{dx}$, and $2b_1 x$ or b_1 for $\frac{db}{dx}$ depending on whether we assume the quadratic or the linear form for b. In the latter case:

$$F(v) = \frac{2a_1x}{v^2}\left(\frac{v-b_1x}{b_1v}\right)$$

so positive, so that $\frac{dp}{dx}=0$ is found in the region where $\frac{dp}{dv}$ is negative. In the former case we get:

$$F(v) = \frac{a_1}{v^2}\left(\frac{v-2b_1x^2}{b_1v}\right)$$

so that $\frac{dp}{dx}=0$ is found in the region were $\frac{dp}{dv}$ is negative (the stable region of the mixtures taken as homogeneous) only if $v > 2b$, which according to the known properties of the isotherm comes to the same thing as that the pressure in the minimum $\left(\frac{dp}{dv}=0\right)$ is positive, or the temperature higher than $\frac{27}{32}$ of the critical temperature.

11. Let us for the present confine ourselves to the supposition of a quadratic function. So in the case which is still under consideration that there is minimum critical temperature and yet $a^2_{12} > a_1a_2$,

no point of intersection of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$ will occur for very low temperature in the region on the right of x_0. For, as VAN DER WAALS has demonstrated (These Proc. June 1908) for such a point of intersection the equations

$$\left.\begin{array}{l} MRT = 2\frac{a}{b}\frac{b}{v}\left(1-\frac{b}{v}\right)^2 = \frac{\frac{da}{dx}}{\frac{db}{dx}}\left\{1-\frac{b\frac{da}{dx}}{2a\frac{db}{dx}}\right\}^2 \\ v = \frac{2a\frac{db}{dx}}{\frac{da}{dx}} \end{array}\right\} \quad . \quad . \quad (1)$$

hold, so for very low temperature a point of intersection is only possible in the neighbourhood of an x, where either $\frac{da}{dx}=0$ or the critical pressure is stationary. Both these possibilities, however are not realised here, for as we shall show later on, a minimum critical temperature at the same time with $a^2_{12} > a_1a_2$ is only possible for a relative position of the lines a and b as indicated in fig. 11, i. e.

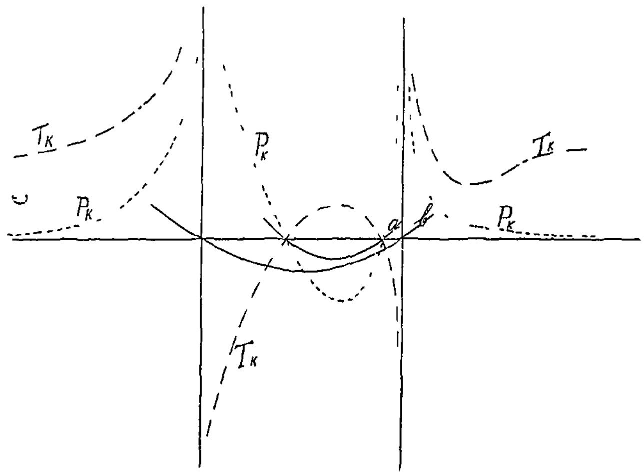

Fig. 11.

the point a_1 on the left of b_1 and $\frac{da}{dx}=0$ on the right of $\frac{db}{dx}=0$. Now for b_1 and b_2 the critical pressure is infinite, for a_1 and a_2 it is zero; also for $x = +\infty$ and $x = -\infty$. The equation $p_k = \frac{a}{b^2}$ being of the fourth degree in x, no more than 4 values of x can ever be found for a certain value of p_k. So no maximum or minimum of the critical pressure can occur on the right of b_1.

Here we interrupt the train of our reasoning for a moment, to show that in the case considered a minimum critical temperature must occur. As the equation:

$$\frac{dT_k}{dx} = \frac{b\frac{da}{dx} - a\frac{db}{dx}}{b^2} = 0$$

gives an equation of the third degree, we might expect that 3 values of x which make T_k stationary, could be found for every system in the complete diagram of isobars. But as for very great values of x always $b\frac{da}{dx} = a\frac{db}{dx} = a_1 b_1 x^3$, one root appears always to lie at infinity, and there are at most two roots for finite x. One of them lies between a_1 and a_2, where T_k becomes $= 0$, the other lies on the right of b_1. For in our case we may write the equation for a and b:

$$a = a_1 (x - x_0)^2 - a_2 \qquad b = b_1 x^2 - b_2$$

so

$$\frac{da}{dx} = 2a_1 (x - x_0) \qquad \frac{db}{dx} = 2b_1 x .$$

$\frac{dT_k}{dx}$ has the sign of $b\frac{da}{dx} - a\frac{db}{dx}$, and so of:

$$2a_1 b_1 x^2 (x - x_0) - 2a_1 b_1 x (x - x_0)^2 = 2a_1 b_1 x^2 x_0 - 2a_1 b_1 x x_0^2$$

so $\frac{dT_k}{dx}$ is positive for high values of x, which proves the presence of a minimum critical temperature in connection with the value $+\infty$ for $b = 0$.

12. Let us now return to our diagram of isobars. We can now represent it fully for low temperatures, now that we have seen that there will be no intersection of $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$ in this case. We have only to add the observation that the value of the pressure on the line $\frac{dp}{dv} = 0$ approaches indefinitely to zero for very great value of x, however small the value of T is, if only not quite zero.

For $\frac{MRT}{v-b}$ is in inverse ratio to x, and $\frac{a}{v^2}$ to x^2. So it follows from this that all the negative isobars starting from the point $x=x_0$, $v=0$ will have the shape we indicated before. The line $p=0$ will intersect the line $\frac{dp}{dv}=0$ at infinite distance. To this isobar, however, also the branch belongs starting from the point $p=0$ on the line $x=x_0$, and also the line $v=\infty$. For a positive pressure the isobar consists of two separate branches. One of them, starting from the point $x=x_0$, $v=0$ remains confined to smaller volumes than $p=0$, the other starting from a point on the line $x=x_0$, arrives somewhere on the vapour branch of $\frac{dp}{dv}=0$, with ascending value of v and x, has a tangent there parallel to the v-axis, and returns again to the line $x=x_0$, now on the other side of the maximum pressure. So we get fig. 10 for the complete course of the isobars.

13. How will this figure be modified with increase of temperature. Let us consider the temperature which is $\frac{27}{32}$ of the minimum critical temperature. From equation (1) on page 802 follows that we may expect a point of intersection at a volume $v=2b$ and a temperature $\frac{27}{32}T_k$ for the mixture with minimum critical temperature $\left(\text{where } a\frac{db}{dx}=b\frac{da}{dx}\right)$. The line $\frac{dp}{dv}=0$ lying at smaller volumes than the line $\frac{dp}{dx}=0$ for very great values of x, as we saw in 10, there must be another point of intersection more to the right. It is clear that these points of intersection have arisen by a contact of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$, and that the two points of intersection have moved from this point of contact in opposite direction. For as the equations for the points of intersection are of the first degree with respect to T and v, it is not possible that two points of intersection lying beside each other move in the same direction; for then we should find different values of T for the same value of x. In the point of intersection lying most to the left the pressure is 0, from which it already follows that there must be another point of intersection; for the pressure finally verging again to zero towards the right, there must be a point between where the pressure has reached its lowest value on

the line $\frac{dp}{dv} = 0$. So this point is really a minimum of pressure. Now the diagram of isobars has changed in this (fig. 12) that a loop-line

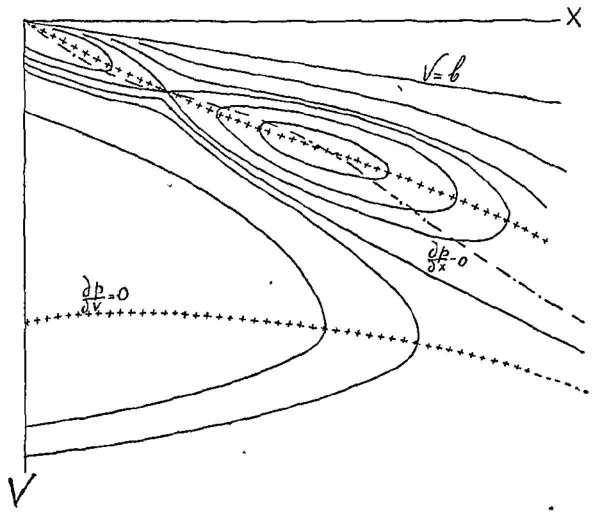

Fig. 12.

has made its appearance, as we see immediately from the fact that the direction of the tangent of the isobar $p=0$, passing through the point of intersection of $\frac{dp}{dv}=0$ and $\frac{dp}{dx}=0$ becomes indeterminate in this point. The two branches of this loop-line start, of course, one from the point $x=x_0$, $v=0$, the other from the point on the line $x=x_0$, where $p=0$. They pursue their course through the double point towards infinity, just as the branches of $p=0$ in figure 10. Now too, the positive isobars have the same course as indicated there. The negative isobars, however, at least part of them, have broken up into two parts, a branch on the left of the mixture with minimum critical temperature, which has again the same course as in fig. 10, and a branch on its right, forming a closed curve round the second point of intersection of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$. Only for isobars for a larger negative value than that in the last-mentioned point there exists only one branch.

It is clear what will be the course for intermediate temperatures. It follows then again from the given equation that the pressure will be negative in the double point lying then at a value of x where $b\frac{da}{dx} > a\frac{db}{dx}$. So we have a loop-line, which itself runs again as a closed line round the second point of intersection of $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$.

14. At a temperature higher than $\frac{27}{32}$ of the minimum critical temperature, there is positive pressure in the double point. For the double point continually proceeds in the same direction; so $\frac{b\frac{da}{dx}}{a\frac{db}{dx}}$ or $\frac{b}{v}$ constantly decreases during this movement and now the expression:

$$\frac{MRT}{MRT_k} = \frac{27}{8}\frac{b\frac{da}{dx}}{a\frac{db}{dx}}\left(1 - \frac{b\frac{da}{dx}}{2a\frac{db}{dx}}\right)^2 = \frac{27}{8}n\left(1-\frac{n}{2}\right)^2$$

has a value 0 for $n = 0$ and $n = 2$, a maximum for $n = \frac{2}{3}$; between $n = 1$ (the x of the minimum critical temperature) and $n = \frac{2}{3}$ the righthand member is, therefore, greater than $\frac{1}{4}$ and so $T > \frac{27}{32}T_k$, so that the pressure in the double point is positive. For $n = \frac{2}{3}$ the double point lies exactly at $T = T_k$ or $v = 3b$, so in the point of $\frac{dp}{dv} = 0$ where this line, which then has split up, has its tangent // v-axis. At still higher temperature the double point of p gets on the vapour branch of $\frac{dp}{dv} = 0$, and disappears at the temperature at which $\frac{da}{dx} = MRT\frac{db}{dx}$ for $x = x_0$, as is indicated in fig. 9. So long as the double point continues to lie on the liquid branch, that branch of the isobar, which comes from $x = x_0$, $v = 0$, passes through the double point, meets the vapour-branch of $\frac{dp}{dv} = 0$ at larger x, where its tangent becomes // v-axis, and then runs back to a point of the line $x = x_0$ for greater value of v than that of the maximum pressure on the straight line mentioned. The other branch of the loop-isobar comes from a point of this line with smaller pressure than the maximum pressure, and having passed the double point it remains at smaller volumes than $\frac{dp}{dx}=0$. The course of the other isobars only undergoes modification as regards the isobars which intersect the line $\frac{dp}{dx}=0$ on the right of the double point. Near the double point positive isobars are found at this temperature. They come from a point on the line $x=x_0$ at larger volume than the largest that the loop-isobar has in common with this line. They are // v-axis on the vapour branch of $\frac{dp}{dv}=0$, then they run back to smaller x, they are again // v-axis on the liquid branch of $\frac{dp}{dv}=0$, and // x-axis on $\frac{dp}{dx}=0$, after which they proceed towards infinity between the last-mentioned line and the loop-isobar. So we have again got isobars here as in the rigthand part of VAN DER WAALS' diagram of isobars (Fig. 13).

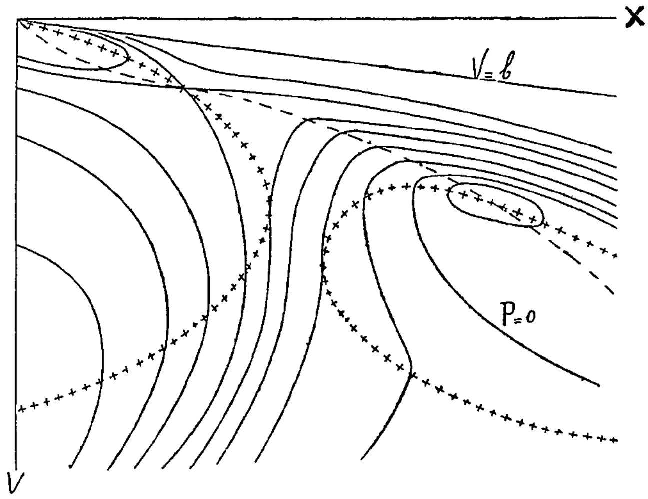

Fig. 13.

When we ascend above the critical temperature, so that $\frac{dp}{dv}=0$ breaks up into a righthand part and into a lefthand part, this involves only that part of the isobars no longer possess the retrograde portion, because the two points of intersection with $\frac{dp}{dv}=0$ have coincided, and then have become imaginary. The last isobar which has the shape described here, is that for $p=0$, the line at infinity included. It then runs from the line $x=x_0$ to the vapour branch of $\frac{dp}{dv}=0$

on the extreme right side of the figure, returns to a point on the liquid branch of $\frac{dp}{dv}=0$, and then intersects $\frac{dp}{dx}=0$ The negative isobars, which have their point of intersection with the liquid branch of $\frac{dp}{dv}=0$ still further to the right, again form closed rings round the second point of intersection of $\frac{dp}{dv}=0$ and $\frac{dp}{dx}=0$. These closed rings do not disappear until the temperature has been raised so high that the value $\frac{27}{32}\frac{a_1+a_2-2a_{12}}{b_1+b_2-2b_{12}}$ has been reached, which may take place either above the minimum critical temperature of the system or not above it, in the first case again either at higher temperature or not at higher temperature than that at which the point of intersection of $\frac{dp}{dv}=0$ and $\frac{dp}{dx}=0$ has shifted from the liquid branch to the vapour branch. So different combinations may present themselves, which, however, do not differ in essential points, and which the reader can easily imagine for himself.

15. At temperatures at which the double point lies on the vapour branch, the loop-isobar, starting from $v=0, x=x_0$ passes first through the liquid branch of $\frac{dp}{dv}=0$, where its direction is // v-axis, then through the double point, after which it reaches the line $x=x_0$. The second branch of the loop-isobar comes from the line $x=x_0$, and after having passed through the double point, it pursues its course always at smaller volumes than $\frac{dp}{dv}=0$ and $\frac{dp}{dx}=0$. In the isobars with higher value of the pressure only this change has come that now a retrograde part appears in the branch at the small volumes for a number of isobars, whereas part of the isobars with lower value than the loop-isobar fail to have the retrograde portion in the branch starting from the line $x=x_0$. They do not get it until the value of the pressure has fallen so low that the righthand part of $\frac{dp}{dv}=0$ is intersected. When the temperature $\frac{a_1+a_2-2a_{12}}{b_1-b_2+2b_{12}}$ has been reached, this part of $\frac{dp}{dv}=0$ has vanished, and so also the retrogression of all these isobars. (fig. 14).

The last modification which our diagram may finally undergo, is when the temperature at which $\frac{da}{dx} = MRT \frac{db}{dx}$ for $x = x_0$, is reached. Our diagram then passes into the usual one, when this is drawn above the critical temperature, and as we have now to deal with the case of fig. 9, into the usual figure after the intersection of

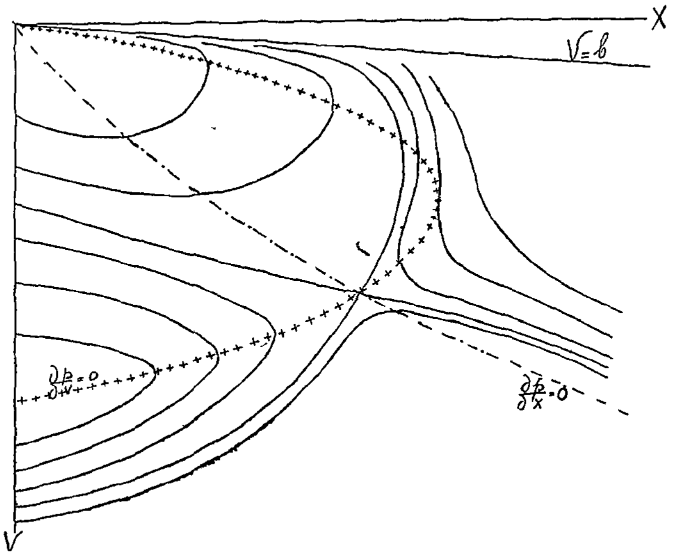

Fig. 14.

$\frac{dp}{dv} = 0$ and $\frac{dp}{dx} = 0$ has disappeared.

16. Now the course of the isobars for the case that a minimum critical temperature occurs at the same time with $a_{12}^2 > a_1 a_2$ is completely determined. Only this complication might possibly be met with — I have at least not succeeded in proving that it is impossible — that besides the discussed contact of $\frac{dp}{dv} = 0$ and $\frac{dp}{dx} = 0$, by which two points of intersection arise, another contact is found. As we saw before the points of contact which then arise will again have to move to opposite sides. Of the four points of intersection which there are in this case, the two inner ones will again coincide at still higher themperature, and give rise to contact. So the difference is confined to the region between the two temperatures of contact, and it has only influence on part of the isobars at small volumes. Thus of the series of isobars which pass round the point with minimum pressure on $\frac{dp}{dv} = 0$ as closed curves, there will

e. g. be one which assumes the shape of a ∞, and the isobars of still smaller value of p will have broken up into two branches each closed in itself (apart from the closed portion starting from $x = x_0$, $v = 0$). C and D (fig. 15) are then the points of intersection which have newly appeared; the complication vanishes again in

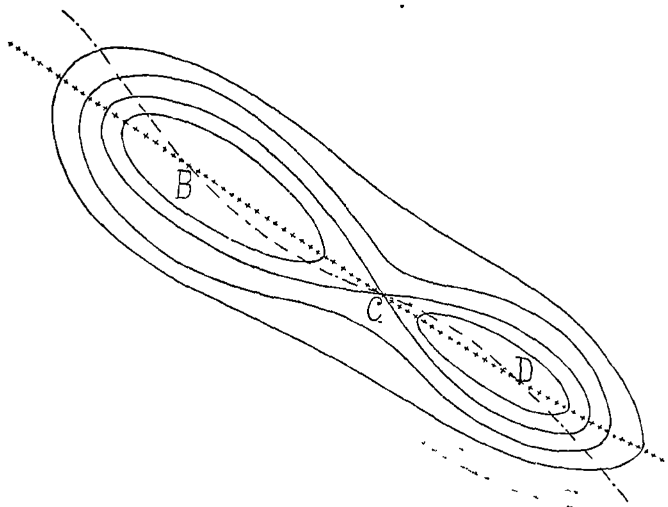

Fig. 15.

consequence of the coincidence of B and C. If the second point of contact should arise on the left of the point of intersection lying to the extreme left instead of on the right of B a similar result would be met with.

17. At first sight the diagrams of isobars obtained above seem to deviate considerably from the figure given by VAN DER WAALS. This is of course partly due to the different course of $\frac{dp}{dx} = 0$. Partly, however, also to the fact that the figure loc. cit. only holds for temperatures, lying between $\frac{27}{32}$ of the critical temperature and the critical temperature itself. Therefore we find the closest resemblance with the figure loc. cit. in our figures for higher temperatures. That the resemblance also continues to exist at lower temperatures is immediately seen when we examine to what changes the figure l. c. is subjected with lowering of the temperature. First of all we have then the temperature:

$$\frac{27}{32}\frac{a_1 + a_2 - 2a_{12}}{b_1 + b_2 - 2b_{12}}.$$

As we saw above another point of intersection of $\frac{dp}{dx} = 0$ and

$\frac{dp}{dv} = 0$ is found on the right below this temperature, round which point of intersection branches of isobars with negative value of the pressure pass as closed curves. For $\frac{27}{32}$ of the minimum critical temperature the loop-isobar will hold for the pressure 0, as we saw above. So it reaches the vapour branch of $\frac{dp}{dv} = 0$ only at infinity (fig, 16). For still lower temperature also the loop-isobar in the case

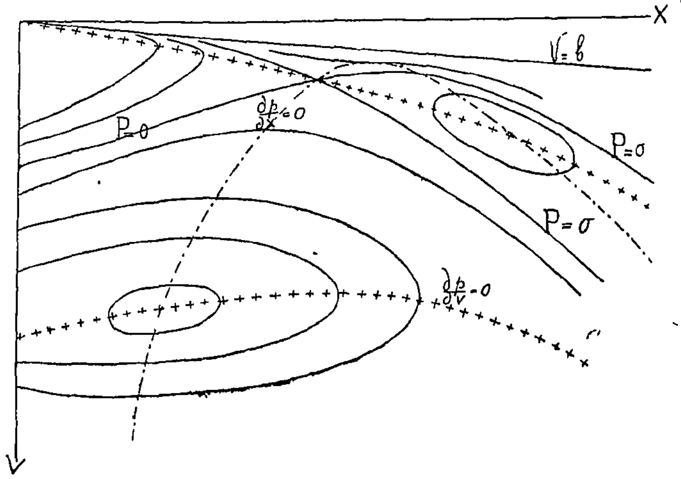

Fig. 16.

of VAN DER WAALS is no longer closed round the point of intersection of $\frac{dp}{dx} = 0$ with the vapour branch of $\frac{dp}{dv} = 0$, but round the third point of intersection. Of course closed rings continue to run round

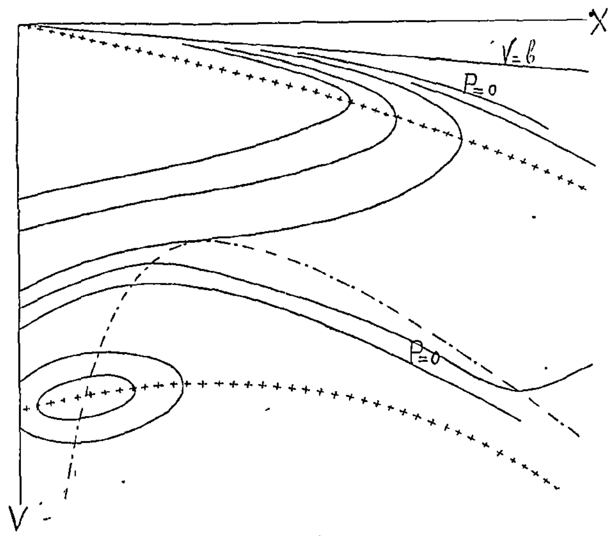

Fig. 17.

the first-mentioned point of intersection, which continues to distinguish the figure from the figures given by us. At still lower temperature the two points of intersection with the liquid branch of $\frac{dp}{dv} = 0$ may coincide. It is true that this clashes with the thesis concerning the contact of $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$, mentioned in the beginning of the previous communication, which gave rise to this investigation, but then this thesis holds only if b is a linear function of x and in this case the said point of intersection on the right does not make its appearance. If the two points of intersection have coincided, the loop-line and the closed rings at small volume have disappeared and only those at large volumes remain. (fig. 17). It is, however, also possible that the points of intersection continue to exist down to the absolute zero point, viz. when a minimum and a maximum occurs in the critical pressure. That this is possible for a quadratic function for b is shown by fig. 18, if we bear in mind

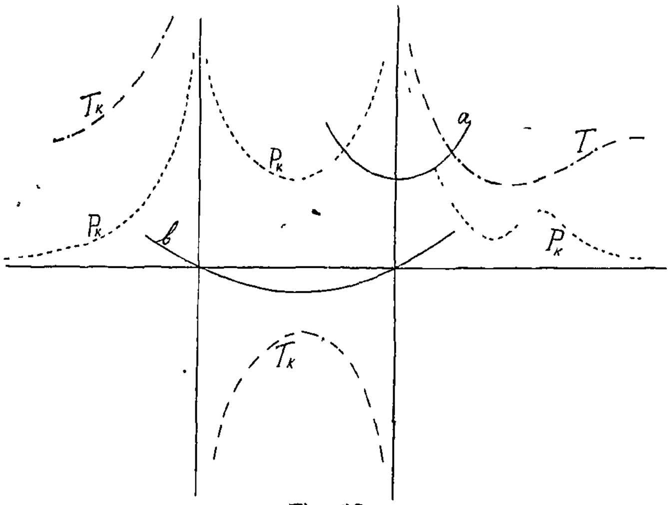

Fig. 18.

that a and so the critical pressure never become zero now. In this case the points of intersection in the liquid branch continue to exist down to the lowest temperatures, their limiting situation is the value for x at which the critical pressure is stationary.

With this exception and with those exceptions which arise by the modified course of $\frac{dp}{dx} = 0$, this diagram and ours harmonize.

In a following communication I hope to show that so long as no maximum critical temperature occurs, no other diagrams of isobars but those discussed are possible in the realizable region (also the unstable one) for whatever values of a, b and a_{12} we combine.