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Physics. — "*Contribution to the theory of binary mixtures.*" By Prof. J. D. VAN DER WAALS.

The theory of binary mixtures, as developed in the "Théorie moléculaire", has given rise to numerous experimental and theoretical investigations, which have undoubtedly greatly contributed to obtain a clearer insight into the phenomena which present themselves for the mixtures. Still, many questions have remained unanswered, and among them very important ones. Among these still unanswered questions I count that bearing on a classification of the different groups of ψ -surfaces. For some binary systems the plait of the ψ -surface has a simple shape. For others it is complex, or there exists a second plait. And nobody has as yet succeeded in pointing out the cause for those different forms, not even in bringing them in connection with other properties of the special groups of mixtures. It is true that in theory the equation of the spinodal curve which bounds the plait, has been given, and when this is known with perfect accuracy, it must be possible to analysis to make the classification. But the equation appears to be very complicated, and it is, especially for small volumes, only correct by approximation, on account of our imperfect knowledge of the equation of state. Led by this consideration I have tried to find a method of treatment of the theory which is easier to follow than the analytical one, and which, as the result proved, enables us to point out a cause for the different shape of the plaits, and which in general throws new light upon other already more or less known phenomena.

Theory teaches that for coexisting phases at given temperature three quantities viz. $-\left(\frac{d\psi}{dv}\right)_{xT}$, $\left(\frac{d\psi}{dx}\right)_{vT}$ and $\psi - v\left(\frac{d\psi}{dv}\right)_{xT} - x\left(\frac{d\psi}{dx}\right)_{vT}$ must be equal. The first of these quantities is the pressure, which we represent by p ; the second is the difference of the molecular potentials or $M_2\mu_2 - M_1\mu_1$, which we shall by analogy represent by q . The third of these quantities is the molecular potential of the first component, which we shall represent by $M_1\mu_1$. Now the points for equal value of p lie on a curve which is continuously transformed with change of the value of p , so that, if we think all the p -curves to be drawn, the whole v,x -diagram is taken up by them. In the same way the points for given value of q lie on a curve which continuously changes its shape with change of the value of q ; and again when all the q -lines have been drawn, the whole v,x -diagram is taken up. Both the p -lines and the q -lines have the property, that through a given point only one p -line, or only one

q -line can be drawn. One single p -line, however, intersects an infinite number of lines of the q -system, and every q -line an infinite number of lines of the p -system. One and the same p -line intersects a given q -line even in several points. However, it will, of course, be necessary, that if two points indicate coexisting phases, both the p -line and the q -line which passes through the first point, passes also through the second point. If we choose a p -line for two coexisting phases, not every arbitrarily chosen value for a q -line will satisfy the condition of coexistence in its intersections with the p -line, because a third condition must be satisfied, viz. that $M_1 \mu_1$ must have the same value. The result comes to this: when all the p -lines and all the q -lines have been drawn and provided with their indices there is one more rule required to determine the points which belong together as indicating coexisting points. So in the following pages I shall have to show, when this method for the determination of coexisting phases is followed: 1. What the shape of the p -lines is, and how this shape depends on the choice of the components. 2. What the shape of the q -lines is, and how this shape depends on the choice of the components. 3. What rule exists to find the pair or pairs of points representing coexisting phases from the infinite number of pairs of points which have the same value of q , when p has been given — or when on the other hand the value of q is chosen beforehand, to find the value of p required for coexistence.

But for the determination of the shape of the spinodal curve the application of the rule in question is not necessary. For this the drawing of the p - and the q -lines suffices. There is viz. a point of the spinodal curve wherever a p -line touches a q -line. We have viz.

$$\text{from } \frac{d^2\psi}{dv^2} \left(\frac{dv}{dx} \right)_p + \frac{d^2\psi}{dv dx} = 0, \text{ and from } \frac{d^2\psi}{dx dv} \left(\frac{dv}{dx} \right)_q + \frac{d^2\psi}{dx^2} = 0 \text{ for } \left(\frac{dv}{dx} \right)_p$$

$$\text{the value } - \frac{\frac{d^2\psi}{dx dv}}{\frac{d^2\psi}{dv^2}} \text{ and for } \left(\frac{dv}{dx} \right)_q \text{ the value } - \frac{\frac{d^2\psi}{dx^2}}{\frac{d^2\psi}{dx dv}}, \text{ and so we may}$$

write the equation of the spinodal curve:

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

So if we are able to derive from the properties of the components of a mixture what the course of the p - and of the q -lines is, we can derive much, if not everything, about the shape of the spinodal curve. And even when the course of these lines can only be predicted qualitatively, and the quantitatively accurate knowledge is wanting,

the quantitatively accurate shape of the spinodal curve will, indeed, not be known, but yet in large traits the reasons may be stated, why in many cases the shape of the plait is so simple as we are used to consider as the normal course, whereas in other cases the plait is more complex, and there are even cases that there is a second plait.

Particularly with regard to the p -lines, it is possible to forecast the course of these lines from the properties of the components. With regard to the q -lines this is not possible to the same extent, but if there is some uncertainty about them, we shall generally have to choose between but few possibilities.

THE COURSE OF THE p -LINES.

In fact the most essential features of the course of the p -lines were already published by me in "Ternary Systems" — and only little need be added to enable us to determine this course in any given case of two arbitrarily chosen components. As $p = -\frac{d\psi}{dv_{xT}}$

and $\left(\frac{dv}{dx}\right)_p = -\frac{\left(\frac{dp}{dx}\right)_{vT}}{\left(\frac{dp}{dv}\right)_{xT}}$, it is required for indicating the course of

these p -lines to know the course of the curves $\left(\frac{dp}{dv}\right)_{xT} = 0$ and $\left(\frac{dp}{dx}\right)_{vT} = 0$.

The former curve has a continuous liquid branch, and a continuous gas branch, at least when T lies below every possible T_k , when we denote by T_k the critical temperature for every mixture taken as homogeneous that occurs in the diagram. If there should be a minimum value of T_k for certain value of x , and T is higher than this minimum T_k , the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$ has split up into two separate curves. In either of them the gas and the liquid branch have joined at a value of $v = v_k$. In this case a tangent may then be traced // to the v -axis to each of these two parts of the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$.

The second curve $\left(\frac{dp}{dx}\right)_{vT} = 0$ is one which has two asymptotes, and which may be roughly compared to one half of a hyperbola. The shape of this curve derived from the equation of state follows from the equation:

$$\frac{MRT \frac{db}{dx}}{(v-b)^2} - \frac{da}{v^2} = 0.$$

If we now always take as second component that with the greatest value of b , so that $\frac{db}{dx}$ is always positive, it appears from the given equation that the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$ cannot possess points for these values of x , for which $\frac{da}{dx}$ is negative. Only at that value of x for which $\frac{da}{dx} = 0$, this possibility begins, but then only if $T = 0$. If

T has a definite value $\frac{da}{dx}$ must be positive, for points of this curve to be possible. For $v = \infty$, $\frac{da}{dx}$ must be $= MRT \frac{db}{dx}$. And the value of x which satisfies this equation, indicates one asymptote of the discussed curve by a line // to the v -axis. If this asymptote has been drawn, we may think the mixtures with decreasing critical temperature to be placed on its left side. And on the right the mixtures with increasing critical temperature do not yet immediately follow. For a separation between the mixtures with decreasing and those with increasing T_k , $\frac{da}{dx}$ must be $= \frac{a}{b} \frac{db}{dx}$; only when $MRT = \frac{a}{b}$ T_k would immediately ascend again on the right of this asymptote; but then T would have to be chosen so high, that it was $\frac{27}{8} T_k$, and for the present at least we shall choose T far below that limit.

That the line $x = c$, where c has the value which follows from $\frac{da}{dx} = MRT \frac{db}{dx}$, is an asymptote, is seen when we think the equation

of the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$ written as follows: $\frac{v^2}{(v-b)^2} = \frac{\frac{da}{dx}}{MRT \frac{db}{dx}}$. As

the value of $\frac{da}{dx}$ becomes larger from left to right, $\frac{v}{v-b}$ must increase from left to right, or $\frac{v}{b}$ decrease. For the value of x , following from $\frac{da}{dx} = MRT \frac{db}{dx}$, $\frac{v}{b}$ is infinite; for larger values of x , $\frac{v}{b}$ decreases

more and more, and as $\frac{v}{b}$ can never become $= 1$, because $\frac{da}{dx}$ cannot become infinite, the curve $v = b$ is the second asymptote. So if x is made to increase more and more, also beyond the values which for a given pair of components are possible in order to examine the circumstances which may occur with all possible systems for which with positive value of $\frac{db}{dx}$ increasing value of T_k is always found, a minimum volume must occur on the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$. So for this point $\left(\frac{d^2p}{dx^2}\right)_{vT} = 0$.

Now that we have described in general outlines the two curves which control the course of the p -lines, we shall have to show in what way they do so.

From

$$\left(\frac{dv}{dx}\right)_{pT} = - \frac{\left(\frac{dp}{dx}\right)_{vT}}{\left(\frac{dp}{dv}\right)_{xT}}$$

follows that to a p -line a tangent may be drawn // x -axis when it passes through the curve $\left(\frac{dp}{dx}\right)_{vT}$, and a tangent // v -axis, when it passes through the curve $\left(\frac{dp}{dv}\right)_{xT}$. But though these are important properties they would be inadequate for a determination of the course of the isobars, if not in general outlines the shape of one of these lines could be given. The line $\left(\frac{dp}{dv}\right)_{xT} = 0$ viz. intersects the line $\left(\frac{dp}{dx}\right)_{vT} = 0$ in two points, and it is these two points which are of fundamental significance for the course of the p -lines. The point of intersection with the liquid branch is viz. for a definite p -line a double point, the second point of intersection being such an isolated point that it may be considered as a p -curve that has contracted to a single point. The surface $p = f(x, v)$ is namely convex-concave in the neighbourhood of the first mentioned point. Seen from below a section // v -axis is convex, and a section // x -axis is concave. A plane, parallel to the v, x -plane touching the p -surface intersects, therefore, this surface in two real lines, according to which p has

the same value. But for the second point of intersection the two sections are concave seen from below — and there are no real lines of intersection. This second point is a real point of maximum pressure. With all these properties, and also with those mentioned before or still to be mentioned, $\frac{d^2a}{dx^2}$ is assumed to be positive. ¹⁾

Now the curve $p = \text{constant}$ passing through the first point of intersection which the curves $\left(\frac{dp}{dv}\right)_{xT} = 0$ and $\left(\frac{dp}{dx}\right)_{vT} = 0$ have in common, is the isobar whose shape we can give, which shape at the same time is decisive for all those following, either for larger or smaller value of p . In the adjoined figure 1 its course is represented. Coming from the left it retains its direction to the right also in the point of intersection with the curve $\left(\frac{dp}{dx}\right)_v = 0$, the convex side all the time turned to the x -axis till it is directed straight downward in the point where it meets the vapour branch of the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$. There it has a tangent // v -axis, and from there it has turned its concave side to the x -axis. When it meets the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$, $\left(\frac{dv}{dx}\right)_p$ is equal to 0 for this as for all isobars. Passing again through the curve $\left(\frac{dp}{dv}\right)_{xT}$, $\left(\frac{dv}{dx}\right)_p$ is again infinitely large, and pursuing its course, it passes for the second time through the double point, and further moves to the right, always passing to smaller values of v , till it has again a tangent // to the axis of x , when it meets the curve $\left(\frac{dp}{dx}\right)_v = 0$ once more, after which it proceeds to larger value of v . It is clear that in the path it describes from the double point till it passes through this point for the second time, it has passed round the point we have called the second point

¹⁾ That the characters of the two points of intersection of the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$ with the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$ are different appears among others from this that when these points of intersection coincide as is the case when these curves touch each other, the quantity $\frac{d^2p}{dv^2} \frac{d^2p}{dx^2} - \left(\frac{d^2p}{dx dv}\right)^2 = 0$. The character of the points of intersection depends on this quantity being positive or negative.

of intersection with the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$, and where maximum pressure is found. In fig. 1 some more isobars have now been drawn besides this one. We obtain the course of the isobars for lower value of p by drawing a curve starting from the left at higher value of v , bearing in mind that two p -lines of different value of p can never intersect, because the p is univalent for given value of x and v . Such an isobar cuts the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$ on the left of the isobar with the double point in two points, where $\left(\frac{dv}{dx}\right)_p = \infty$, then passes through the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$ in a point where $\left(\frac{dv}{dx}\right)_{vT} = 0$, and has then also on the right of the said isobar again two points of intersection with the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$, in which points of intersection again $\left(\frac{dv}{dx}\right)_{pT} = \infty$.

An isobar of somewhat higher value of p has split up into two isolated branches. One of them starts on the right at somewhat smaller value of v ; further this branch follows the course of the isobar with the loop, but must not cut it. Arrived in the neighbourhood of the double point it is always obliged to remain at small volumes; there it meets the curve $\left(\frac{dp}{dv}\right)_v = 0$, and it has $\left(\frac{dv}{dx}\right)_p = 0$. From this point it proceeds to smaller volumes, till a new meeting-point with the same curve causes this branch again to turn to larger volumes. But the second branch of this isobar of higher value of p is entirely inclosed within the loop of the loop-isobar. Such a branch forms a closed curve surrounding the point which we have called the second point of intersection of the curves $\left(\frac{dp}{dv}\right)_x = 0$ and $\left(\frac{dp}{dx}\right)_v = 0$. Such a closed branch passes twice through $\left(\frac{dp}{dx}\right)_v = 0$, and also twice through $\left(\frac{dp}{dv}\right)_x = 0$, and has again in the first cases $\left(\frac{dv}{dx}\right)_p = 0$, in the second points of intersection $\left(\frac{dv}{dx}\right)_p = \infty$.

With ascending value of p the detached portion of the p -line contracts more and more, till it has contracted to a single point. So at still higher value of p only one single branch of the p -line remains.

A similar remark must be made for the curves of lower value of p . The smallest value of p for gas volumes is of course $p = 0$, but this limit does not exist for the minimum pressure of the mixtures with given value of x . For this we know that also values of p may occur which are strongly negative. For values of p which are negative, the p -line has again divided into two disjointed portions, viz. a portion lying on the left in the diagram, which is restricted to volumes somewhat larger and somewhat smaller than that of the liquid branch of the curve $\left(\frac{dp}{dv}\right)_x = 0$, and a similar portion lying on the right in the diagram.

Also on the locus of the points of inflection of the isobars the given diagram can throw light. So it is evident in the first place, that between the two branches of the curve $\left(\frac{dp}{dv}\right)_x = 0$ starting from the double point, both on the left and on the right a connected series of points is found where $\left(\frac{d^2v}{dx^2}\right)_p = 0$. If the curve $\left(\frac{dp}{dv}\right)_x = 0$ itself should possess a double point, which is the case when T has exactly the value of T_L minimum, this locus of the points of inflection of the p -lines passes through this double point, and when the curve $\left(\frac{dp}{dv}\right)_x = 0$ has split up into two separate portions, as is the case for still higher value of T , then those points of the two portions where $\frac{dv}{dx} = \infty$ belong to this locus. It is also apparent from the diagram that two more series of points start from the double point, one on the right and one on the left, as locus of the points of inflection, and that these run to smaller volumes.

An isobar with somewhat larger value of p than that of the loop-shaped isobar has a tangent // to the x -axis where it passes through the curve $\left(\frac{dp}{dx}\right)_v = 0$. On the right and on the left of that point it turns its concave side to the x -axis, whereas at larger distance it must again turn its convex side to it on both sides. So there start from the double point four branches on which $\left(\frac{d^2v}{dx^2}\right)_p = 0$. It is also easy to see that the branch which moves to the right towards smaller volumes, must pass through that point of the curve $\left(\frac{dp}{dx}\right)_v = 0$ where the tangent is // x -axis. For an isobar which passes through

the curve $\left(\frac{dp}{dx}\right)_v = 0$ on the left of this point, turns its concave side to the x -axis, but when it passes for the second time through the said curve on the right of the point, its convex side. Hence an isobar where these two intersections have coincided, has its point of inflection in the point itself. If we wish to divide all the v, x -diagram into regions where $\left(\frac{d^2v}{dx^2}\right)_p$ is either positive or negative, it must be borne in mind that also the two branches of line $\left(\frac{dp}{dv}\right)_x = 0$ themselves form the boundaries for these regions, because on that line $\left(\frac{dv}{dx}\right)_p = \infty$.

In all this $\frac{d^2a}{dx^2}$ is supposed to be positive. For on the contrary the course of the line $\left(\frac{dp}{dx}\right)_v = 0$, to which we could now assign an existence on the right of the asymptote which is given by $MRT \frac{db}{dx} = \frac{da}{dx}$, would be directed to the left of this asymptote, when $\frac{d^2a}{dx^2}$ should be negative, so if $2a_1$, could be $> a_1 + a_2$. For as

$$\left(\frac{v}{v-b}\right)^2 = \frac{\frac{da}{dx}}{MRT \frac{db}{dx}}, \text{ the value of } \frac{v}{b} \text{ decreases only, when } \frac{da}{dx} \text{ increases.}$$

If we put $a = A + 2Bx + Cx^2$, and so $\frac{da}{dx} = 2(B + Cx)$, it appears that with C negative x must decrease in order to make $\frac{da}{dx}$ increase.

For the points of this line p would then possess a minimum for given value of v , and so $\frac{d^2p}{dx^2}_v$ would be positive. From this follows then that the two points of intersection of this line with the curve $\left(\frac{dp}{dv}\right)_x = 0$ have interchanged rôles. The point of intersection with the smallest volume represents then a real minimum of p , and will have the same significance for the course of the p -lines as the second point of intersection has, when $\frac{d^2a}{dx^2}$ is positive. And the point of intersection

with the smallest volume has now become double point. I have, however, omitted the drawing of this case 1. because most likely the case does not really occur, and 2. because the drawing may easily be found by reversing the preceding one. There are e.g. with the solution of salts in water cases which on a cursory examination present some resemblance with the assumption $\frac{d^2a}{dx^2}$ negative, but which yet are brought about by influences perfectly different from the fact of a negative value for $\frac{d^2a}{dx^2}$.

Such a diagram for the case $\frac{d^2a}{dx^2}$ negative, though, would quite fall in with the right side of fig. 1. As in the given figure T_k increases with x on the right side, and there is a maximum value of T_k on the supposition $\frac{d^2a}{dx^2}$, fig. 1 might be still extended to the right till such a maximum T_k was reached. But then we should also have to suppose that a value of x could exist or rather a mixture for which at a certain value of x the quantity $\frac{d^2a}{dx^2}$ reverses its sign.

Every region of fig. 1 of certain width which is taken parallel to the v -axis can now be cut out for $a_1 + a_2 - 2a_{12}$, positive, to denote the course of the isobars. Regions on the left side indicate the course of the isobars for mixtures for which with increasing value of b the critical temperature decreases — regions on the right side for mixtures for which with increasing value of b the critical temperature increases — the middle region with the complicated course of the isobars when there is a minimum T_k . The left region would be compressed to an exceedingly small one if we wished to exclude the case $\frac{da}{dx}$ negative or $\frac{da}{dx} = 0$. We do so when putting $a_{12} = \sqrt{a_1 a_2}$. On such a suppo-

sition a minimum T_k is still possible, but the left region must then have an exceedingly narrow width. There is, however, no reasonable ground for the supposition $a_1 a_2 = a_{12}^2$. There would be, if the quantity a for the different substances depended only on the molecular weights, and so $a = \epsilon m^2$ held for constant value of ϵ . If the attraction, just as with NEWTON's attraction, is made to depend on the mass of the molecules, and so if we put $a_1 = \epsilon_1 m_1^2$, and also $a_2 = \epsilon_2 m_2^2$, it appears that ϵ_1 and ϵ_2 are not equal. If we now put $a_{12} = \sqrt{a_1 a_2}$, we put $a_{12} = m_1 m_2 \sqrt{\epsilon_1 \epsilon_2}$. What reasonable ground is there now for the sup-

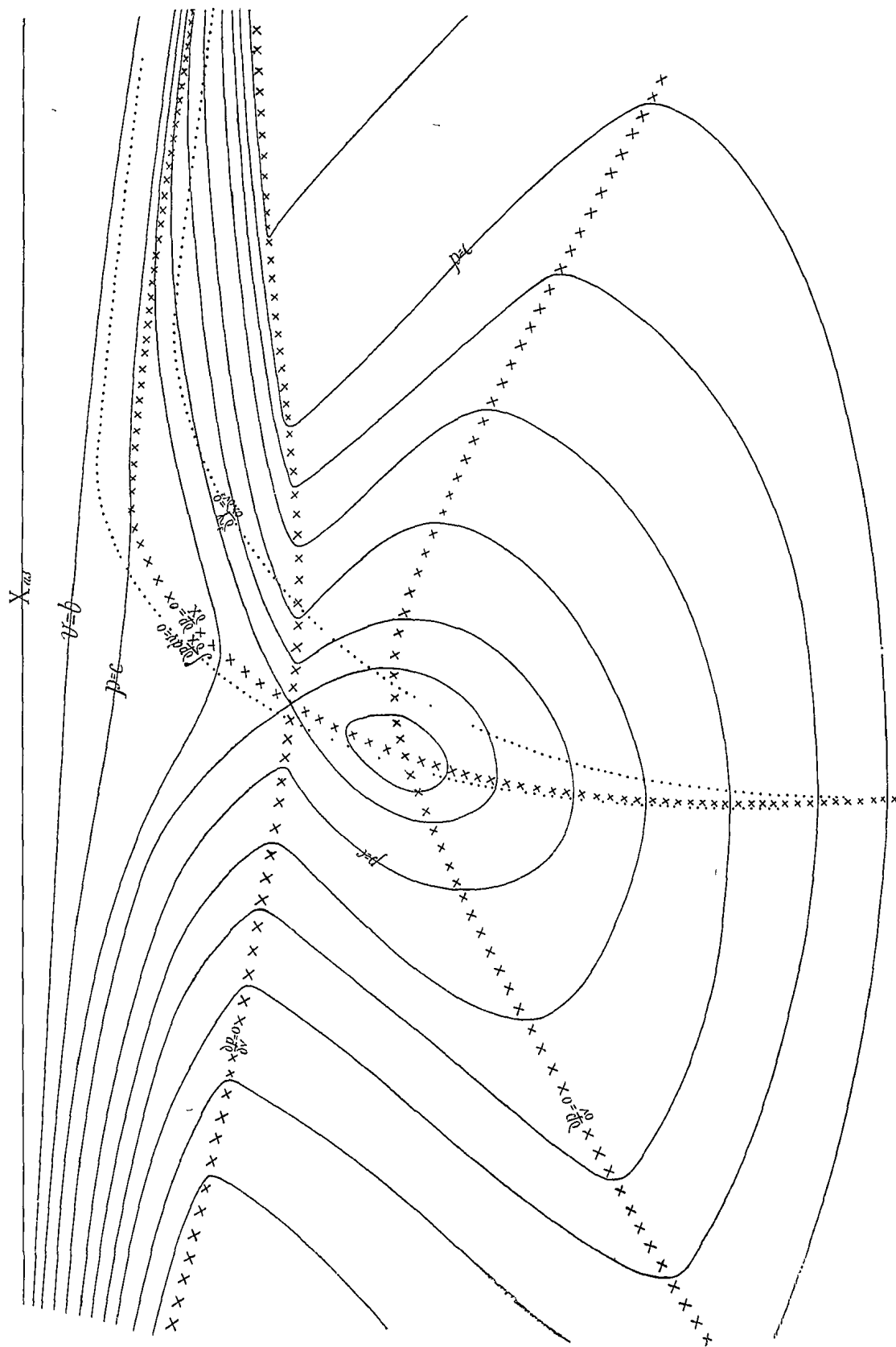


Fig 1.

position that if there is a specific factor ϵ_1 for the mutual attraction of the molecules of the first kind of which we do not know with what property of these molecules it is in connection, and if there is also a perfectly different factor ϵ_2 for the mutual attraction of the second substance, we must not represent the specific factor for the attraction of the different molecules inter se by ϵ_{12} , but by $\sqrt{\epsilon_1 \epsilon_2}$. It is true that this supposition renders the calculations simpler; I had already drawn attention to this in my *Théorie Moléculaire* (Cont. II, p. 45). But whether the calculations are somewhat more or somewhat less easy does not seem a sufficient ground, after all, to introduce a supposition which involves that naturally a great number of possible cases, among others also for the course of the spinodal line, are excluded. If we put all possibilities for the value of a_{12} , then $\frac{da}{dx}$ can also be $= 0$, viz. for $\frac{x}{1-x} = \frac{a_2 - a_{12}}{a_1 - a_{12}}$. We need not go so far however, to give sufficient width also to the left region.

THE COURSE OF THE q -LINES.

The value of $\left(\frac{d\psi}{dx}\right)_v = q$ is found from the value of ψ :

$$q = MRT l \frac{x}{1-x} + \int_v^{\infty} \left(\frac{dp}{dx}\right)_v dv.$$

For $x=0$ this expression is negatively infinite, for $x=1$ it is positively infinite, so that we have $q_0 = -\infty$ and $q_1 = +\infty$.

But it follows also from the equation of state that for all values of x the value of $\int_v^{\infty} \left(\frac{dp}{dx}\right)_v dv$ is also positively infinite for the line $v=b$.

It is true that for such small volumes the equation of state $p = \frac{MRT}{v-b} - \frac{a}{v^2}$ is not accurate when b is not made to depend on v , and the quasi association in the liquid state is left out of account,

and that the conclusion: $\int_v^{\infty} \left(\frac{dp}{dx}\right)_v dv$ is infinitely large for v equal to the

limiting volume, calls for further consideration before we may accept this as an incontestable truth. But it seems to me that simple considerations lead to this conclusion. For the limiting volume p is infinitely great, and if b increases with x , $\left(\frac{dp}{dx}\right)_v$ is infinitely large

of higher order, whereas $\int_v^\infty \left(\frac{dp}{dx}\right)_v dv$ can again diminish the order of infinity by a unit, because the factor of dv has this higher order of infinity only for an infinitesimal value of dv . But still the thesis remains true that $\int_v^\infty \left(\frac{dp}{dx}\right)_v dv$ is infinitely great for $v = b$.

So there is strong asymmetry in the shape of the q -lines. Whereas $q = -\infty$ holds for $x=0$ and every value of $v > b_1$, $q = +\infty$ holds all over the line of the limiting volumes, and for all volumes on the line $x=1$ which are larger than b_2 . We derive immediately from this, that all the q -lines without exception start from the point $x=0$ and $v=b_1$. In this point the value of q is indefinite, as also follows from the value of q as it is given by the approximate equation of state, viz.:

$$q = MRT l \frac{x}{1-x} + MRT \frac{\frac{db}{dx}}{v-b} - \frac{dv}{v}.$$

It also follows from the approximate equation of state that at their starting point all the q -lines touch the line $v=b$, of course with the exception of the line $q = -\infty$. For we derive from

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

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

or

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

For $\frac{d^2\psi}{dx^2}$ the approximate equation of state yields:

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

We already found the value of $-\frac{d^2\psi}{dx dv} = \left(\frac{dp}{dx}\right)$ above. For $\left(\frac{dv}{dx}\right)_q$ we find therefore:

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

If we multiply numerator and denominator by $(v-b)^2$ and if we put $v=b$, we find for the starting point of the q -lines $\left(\frac{dv}{dx}\right) = \frac{db}{dx}$ at least if we can prove that $\frac{(v-b)^2}{x}$ is equal to zero for $x=0$ and $v=b_1$. To show this, we put $b=b_1 + \beta x + \gamma x^2$, and so $v-b = (v-b_1) - x\beta - \gamma x^2$, and then we find for $(v-b) \frac{v-b}{x}$ the value:

$$(v-b) \left\{ \frac{v-b_1}{x} - \beta - \gamma x \right\}.$$

The term $\frac{v-b_1}{x}$ is indefinite, but nevertheless the given value multiplied by $v-b$ is really equal to zero. This result, too, is still to be subjected to further consideration, because it has been obtained by the aid of the equation of state, which is only known by approximation. And then I must confess that I cannot give a conclusive proof for this thesis. But I have thought that I could accept it with great certainty, because in all such cases where a whole group of curves starts from one vertex of an angle, e. g. for the lines of distillation of a ternary system, I have found this thesis confirmed that then they all touch one side of the angle. Only in very exceptional cases the thesis is not valid.

Moreover, the theses which I shall give for the further course of the q -lines, are independent of the initial direction of these lines. Only, the q -lines themselves present a more natural course when their initial direction is the indicated one than in the opposite case.

From the value given above for $\left(\frac{dv}{dx}\right)_q$ follows that they have a tangent // v -axis, when $\left(\frac{dp}{dx}\right)_v = 0$, and a tangent // x -axis, when $\frac{d^2\psi}{dx^2} = 0$. Hence they have a very simple shape in a region where the lines $\left(\frac{dp}{dx}\right)_v = 0$ and $\frac{d^2\psi}{dx^2} = 0$ do not occur. Starting from the point $x=0$ and $v=b_1$ they always move to the right and towards

larger volume, and $\left(\frac{dv}{dx}\right)_q$ is always positive. Therefore $\left(\frac{dp}{dx}\right)_v$ and as will presently appear, $\frac{d^2\psi}{dx^2}$ are always positive in such a region. As v becomes greater the value of q approaches to $MRTl \frac{x}{1-x}$, and for very large value of v the q -lines may be considered as lines parallel to the v -axis, for which the distribution over the region from $x=0$ to $x=1$ is symmetrical. The lines for which q is negative, extend therefore from $x=0$ to $x=\frac{1}{2}$ and for $x=\frac{1}{2}$ the value of $q=0$. It will only appear later on that yet in their course probably two points of inflection always occur for small volumes, a fact to which my attention was first drawn by a remark of Dr. KOHNSTAMM, who had concluded to the presence of such points of inflection in the q -lines from perfectly different phenomena.

But as soon as the line $\left(\frac{dp}{dx}\right)_v=0$ is present (the case that also $\frac{d^2\psi}{dx^2}$ may be $=0$ will be discussed later on), a new particularity makes its appearance in the course of the q -lines. A q -line, viz., which cuts this locus, has a tangent // v -axis in its point of intersection, and reverses its course in so far that further it does not proceed to higher value of x , but runs back to smaller value — so that $\left(\frac{dv}{dx}\right)_q$, which is always positive in the beginning, is henceforth negative. From that point where they intersect the line $\left(\frac{dp}{dx}\right)_v=0$ and where $\left(\frac{dv}{dx}\right)_q$ may be considered negatively infinite, this quantity becomes smaller negative. Still for $v=\infty$, the q -line must again run parallel v -axis. So there must again be a point of inflection in the course of the q -line. In fig. 2 this course of the q -lines has been represented, both in the former case when they do not intersect the curve $\left(\frac{dp}{dx}\right)_v$, and when they do so. In the latter case they have already proceeded to a higher value of x in their course than that they end in. They end asymptotical to a line $x=x_c$, and at much smaller volume they also pass through a point $x=x_c$. The point at which with smaller volume they have the same value of x as that with which they end, lies on a locus which has a shape presenting great resemblance with the line $\left(\frac{dp}{dx}\right)_v=0$. The value,

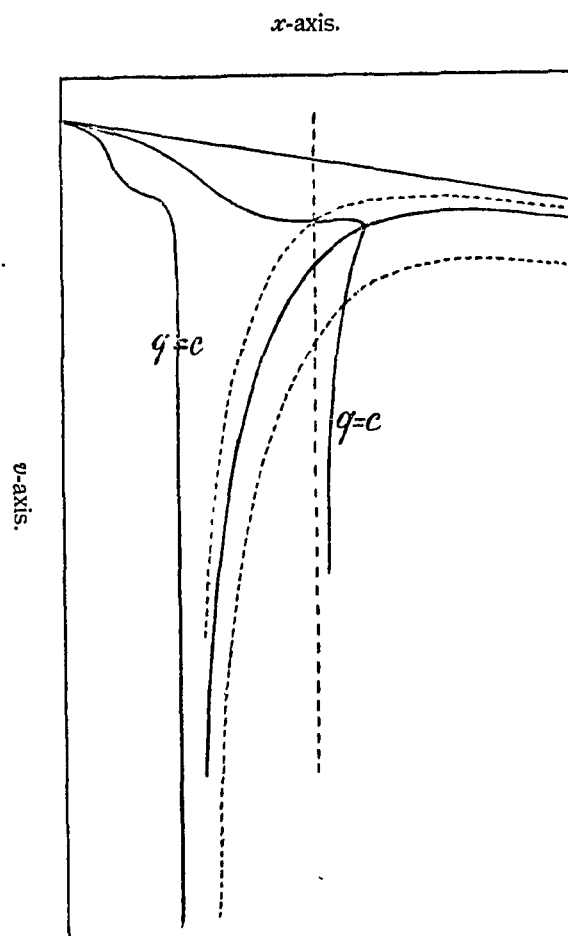


Fig. 2.

for the points of this locus may be derived in the following way.

If we write $\psi = MRT \{ (1-x) \log (1-x) + x \log x \} + \int_v^{\infty} p dv$

then $\left(\frac{d\psi}{dx} \right)_v = q = MRT l \frac{x}{1-x} + \int_v^{\infty} \left(\frac{dp}{dx} \right)_v dv$.

At infinite volume the value of $q = MRT l \frac{x}{1-x}$ as we saw above. The locus under consideration must therefore be determined by

$\int_v^{\infty} \left(\frac{dp}{dx} \right)_v dv = 0$. Hence on the line $x =$ the final value, a point must

be found such that, proceeding along that same x -line, $\int_v^{\infty} \left(\frac{dp}{dx}\right)_v dx = 0$.

So from this follows immediately 1. that the points of the said locus restrict themselves to those values of x in which the curve $\left(\frac{dp}{dx}\right)_v = 0$ occurs, 2. that the points must be found with smaller volumes than those of $\left(\frac{dp}{dx}\right)_v = 0$. For such points with smaller volume is viz.

$\left(\frac{dp}{dx}\right)_v$ positive, and for points with greater volume negative — however when the volume may be considered as a gas volume this négative value has an exceedingly small amount. And even without

drawing up the equation $\int_v^{\infty} \left(\frac{dp}{dx}\right)_v dv = 0$, we conclude that the said locus

has the same x -asymptote as $\left(\frac{dp}{dx}\right)_v = 0$ itself, and is further to be

found at smaller volumes. Hence it will also have a point where its tangent runs // x -axis. There is even a whole series of loci to be given of more or less importance for our theory, which have a

course analogous to that of $\left(\frac{dp}{dx}\right)_v = 0$ and $\int_v^{\infty} \left(\frac{dp}{dx}\right)_v dv = 0$.

The latter is obtained from $\left(\frac{dp}{dx}\right)_v$ by integration with respect to v ; all the differential quotients with respect to v of the same function $\left(\frac{dp}{dx}\right)_v$ put equal to 0 have an analogous course — thus $\frac{d^2p}{dx dv} = 0$ which is a locus of great importance for our theory. That it has the same x asymptote as $\left(\frac{dp}{dx}\right)_v = 0$ itself, and that all its other points are to be found at higher value of v , follows immediately from the following consideration. For a point of the line $\left(\frac{dp}{dx}\right)_v = 0$ the value of $\left(\frac{dp}{dx}\right)_v = 0$. For points of the same x and smaller v this value is positive — but for points with larger v negative. For $v = \infty$ this negative value has, however, again returned to 0. So there must have been a maximum negative value for a certain volume larger than that

for which this value $= 0$. These are the points for which $\frac{d^2 p}{dx dv} = 0$.

For smaller value of the volume $\frac{d^2 p}{dx dv}$ is therefore negative — on the other hand positive for larger volumes. The approximate equation of state yields for the loci mentioned and for following loci these equations:

$$\frac{\frac{db}{dx}}{v-b} = \frac{\frac{da}{dx}}{v} \quad \text{for} \quad \int_v^{\infty} \frac{dp}{dx} dv = 0$$

$$\frac{\frac{db}{dx}}{(v-b)^2} = \frac{\frac{da}{dx}}{v^2} \quad \text{for} \quad \left(\frac{dp}{dx} \right)_v = 0$$

$$\frac{\frac{db}{dx}}{(v-b)^3} = \frac{\frac{da}{dx}}{v^3} \quad \text{for} \quad \left(\frac{d^2 p}{dx dv} \right) = 0.$$

And so forth.

But let us now return after this digression to the description of the shape of the q -lines. Whenever a q -line passes through the locus

$\int_v^{\infty} \left(\frac{dp}{dx} \right) dv = 0$, the asymptote to which it will draw near at infinite volume is known by the value of x for that point of intersection. For the present it does, indeed, pursue its course towards higher value of x , but when it meets the locus $\left(\frac{dp}{dx} \right)_v = 0$, it has the highest value of x , and a tangent // v -axis. From there it runs back to smaller value of x .

And this would conclude the discussion of the complications in the shape of the q -lines, if in many cases for values of T at which the solid state has not yet made its appearance, there did not exist another locus, which can strongly modify the shape of the q -lines, and as we shall see later on, so strongly that three-phase-pressure may be the consequence of it.

The quantities $\frac{d^2 \psi}{dv^2}$ and $\frac{d^2 \psi}{dx^2}$ occur in the equation of the spinodal curve in the same way. It may be already derived from this that the existence of the loci $\frac{d^2 \psi}{dv^2} = 0$ and $\frac{d^2 \psi}{dx^2} = 0$ will have the same significance for the determination of the course of the spinodal line.

That as yet our attention has almost exclusively been directed to $\frac{d^2\psi}{dv^2} = 0$ is due to the fact that we know with certainty that a given binary mixture furnishes points for the latter locus for values of T below T_k for that mixture, whereas the conditions for the existence of a locus $\frac{d^2\psi}{dx^2} = 0$ are not known — and it might be suspected that this remained confined to temperatures so low that the solid state would have set in, and so the complications which would be caused by this, could not be observed. That such a supposition is not quite unfounded may still be safely concluded from the behaviour of many mixtures, which quite answer to the considerations in which the curve $\frac{d^2\psi}{dx^2}$ is left out of account. But that the behaviour of mixtures for which more complicated phenomena occur, cannot be accounted for but by taking into consideration that $\frac{d^2\psi}{dx^2}$ can be $= 0$, seems also beyond doubt to me.

The approximate equation of state gives for this quantity the following value:

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

which I shall still somewhat simplify by assuming that b depends linearly on x , and so $\frac{d^2b}{dx^2} = 0$. We can easily derive from this form that if $\frac{d^2\psi}{dx^2}$ can be $= 0$, this will be the case in a closed curve. At the boundaries of the v, x -diagram $\frac{d^2\psi}{dx^2}$ is certainly positive. For $x = 0$ and $x = 1$ even infinitely great. Also for $v = b$. And for $v = \infty$ it reduces to $\frac{MRT}{x(1-x)}$, the minimum value of which is equal to $4 MRT$. That, if only T is taken low enough, it can be negative, at least if $\frac{d^2a}{dx^2}$ is positive, is also obvious. At exceedingly low value of T it can take up a pretty large part of the v, x -diagram, which must especially be sought in the region of the small volumes. With rise of temperature this locus contracts, and at a certain maximum temperature for its existence, it reduces to a single point. So it is no longer found above a certain temperature.

(To be continued).