

Citation:

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direction of channel rays which he led through it, he photographed at the same time 1. the normal lines of the hydrogen at rest and 2. the strongly shifted lines of the hydrogen-ions in motion. ¹⁾

And so finally it appears that the relative tranquillity of the sun, never disturbed by terrible eruptions, as has been proved so clearly by numerous important solar phenomena and has been demonstrated especially also in the last year by the rotation-investigations of ADAMS, HALE and FOX, ²⁾ is not even in contradiction with a DOPPLER shifting of the spectral lines of the Protuberances.

Delft, the 1st of January, 1909.

Physics. — “*On the course of the isobars of binary mixtures.*”

By Prof. PH. KOHNSTAMM. Communicated by Prof. J. D. VAN DER WAALS.

1. In these Proceedings of June 27th 1908 VAN DER WAALS showed that only if $a^2_{12} < a_1 a_2$ the curves $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$ can touch for volumes larger than $3b$, the critical volume of the mixture taken as homogeneous. On the supposition $a_1 a_2 = a^2_{12}$ the point of contact lies at a value $v = b$. Now at higher temperature the well-known diagram of isobars (These Proc. IX p. 630) leads to the intersection of the two branches of $\frac{dp}{dv} = 0$ on the line $\frac{d^2p}{dv dx} = 0$, which takes place at the minimum critical temperature of the system under discussion. Then the line $\frac{dp}{dv} = 0$ divides into two branches, which we can now denote as the lefthand branch and the righthand branch. The lefthand branch necessarily intersects the line $\frac{dp}{dx} = 0$ in two points, and as it contracts more and more, while the line $\frac{dp}{dx} = 0$ moves towards the right with increase of temperature — the asymptote of this locus being given by $\frac{da}{dx} = MRT \frac{db}{dx}$ — contact must take place, and that for a volume larger than that for which the line

¹⁾ STARK: *Astroph. Journ.* Dec. 1906, p. 362.

²⁾ ADAMS: *Astroph. J.* November 1907, April 1908. — HALE: *ibid.* April 1908. — FOX: *ibid.* Sept. 1908.

$\frac{dp}{dv} = 0$ has its tangent parallel to the v -axis, and which is therefore larger than $3b$. So it would seem to follow from this diagram of isobars, in connection with the just-mentioned theorem of VAN DER WAALS that the possibility of a minimum critical temperature is excluded on the supposition $a_1 a_2 = a_{12}^2$. However, already in his *Théorie Moléculaire* VAN DER WAALS derived the condition for the existence of a minimum critical temperature, viz. :

$$\frac{a_{12}}{b_{12}} < \frac{a_1}{b_1} \quad \text{and} \quad \frac{a_{12}}{b_{12}} < \frac{a_2}{b_2} \quad (1)$$

It is clear that it is easy to satisfy this condition also in the case of $a_{12}^2 = a_1 a_2$, e.g. — if we assume ¹⁾ $2b_{12} = (b_1 + b_2)$ — by the values $b_2 = 3b_1$ and $a_2 = 3a_1$, from which $b_{12} = 2b_1$, $a_{12} = a_1 \sqrt{3}$, so that the two conditions (1) become :

$$\frac{1}{2} \sqrt{3} < 1 .$$

Now it is true that the case will not easily occur that of two substances which have the same critical temperature, the one has molecules three times as large as those of the other, and a physical theory which does not intend to investigate all mathematically possible combinations of a 's and b 's, but only those which really occur, need perhaps hardly consider this point. It would indeed be very desirable for us to have an insight into the way in which the a 's and b 's of simple substances are connected, and for mixtures into the way in which a_{12} is connected with the a 's of the components, so that the theory of the mixtures need only reckon with realisable combinations. Now, however, we do not possess this knowledge, and it seems hardly possible as yet to indicate in what direction such an insight might be gained. Under these circumstances it seems to me most advisable to develop as completely as possible the conclusions which proceed from the different possible suppositions for the dependence of a_{12} on a_1 and a_2 , and to compare these results with the results of observation, in order to try and get an indication in this way of the last-mentioned dependence. No doubt we shall treat a great many suppositions and combinations in this way which will appear to be of no physical signification, but it seems to me that under the given circumstances this difficulty is unavoidable. In this sense the following investigations concerning diagrams of isobars, deviating from those examined up to now and cited above, are to be considered.

¹⁾ In fact we must do so, because the theorem of VAN DER WAALS mentioned only holds for this supposition.

2. It appears from the fact mentioned in 1 viz. that the diagram of isobars of fig. 1 loc. cit. in connection with the theorem of VAN DER WAALS mentioned excludes the possibility of a minimum critical temperature for the case $a_{12} = a_1 a_2$, whereas after all also on this supposition a minimum critical temperature is not impossible, that the diagram of isobars mentioned is not the only one possible. Now the shape of this diagram is in the first place controlled by the line $\frac{dp}{dx} = 0$, and the question suggests itself if in general another shape of this line is also conceivable. In the determination of its course it was derived from the equation :

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

that an asymptote must exist for the value of x determined by :

$$\frac{da}{dx} = MRT \frac{db}{dx}$$

and that to the right of this point everywhere a positive value of v greater than b is to be found satisfying this equation. In this it has been tacitly assumed that for the value of x , for which $\frac{da}{dx} = MRT \frac{db}{dx}$, b is still positive; for if b were negative at this place, only a high *negative* value of v could satisfy for the values of x somewhat larger than that for which $\frac{da}{dx} = MRT \frac{db}{dx}$, and hence the course of $\frac{dp}{dx} = 0$ would become an altogether different one. So though naturally that value of x for which b becomes $= 0$, can never lie within the realisable part of the diagram of isobars, it yet appears that the situation of this point can determine the course of $\frac{dp}{dx} = 0$ and with it of the isobars in the realisable region.

3. In the complete (extended) diagram of isobars such a point must probably always occur. This is self-evident if we should be justified in considering the dependence of b on x as linear, and it is also easy to show it if we assume LORENTZ'S well-known formula for b_{12} . For then :

$$b_{12} = \left(\frac{v b_1 + v b_2}{2} \right)^2$$

and we have to prove that this value is larger than $\sqrt{b_1 b_2}$. If we now put $b_2 = n^2 b_1$, the condition which is to be satisfied, is:

$$\frac{n^6 + 3n^4 + 3n^2 + 1}{8} > n^3$$

or

$$n^6 + 3n^4 - 8n^3 + 3n^2 + 1 > 0$$

or

$$(n-1)^2 (n^4 + 2n^3 + 6n^2 + 2n + 1) > 0.$$

It is clear that for positive values of n this condition is always fulfilled, so that $b_{12}^2 > b_1 b_2$, and the equation:

$$b_1 (1-x)^2 + 2b_{12} x (1-x) + b_2 x^2 = 0$$

has always real roots.

4. It has now been assumed in the general diagram of isobars (loc cit.) that these roots always lie on the leftside of that value of x for which $\frac{da}{dx} = 0$. To what change will this diagram be subjected in the opposite case? We begin with determining the course of $\frac{dp}{dx} = 0$ in this case. So as $\frac{da}{dx}$ is positive, according to our supposition, for that value of x for which $b = 0$, we can always think the temperature so low that for this value of x , which we shall call x_0 .

$$n = \frac{MRT \frac{db}{dx}}{\frac{da}{dx}} < 1$$

Then we get for the course of $\frac{dp}{dx} = 0$ in the neighbourhood of x_0

$$\frac{v-b}{v} = \pm \sqrt{n} \text{ or } v(1 \pm \sqrt{n}) = b \quad \dots (2)$$

Now the value of b is positive for somewhat higher value of x than x_0 , whereas b becomes negative for somewhat smaller value of x . So we see that two branches of $\frac{dp}{dx} = 0$ pass through the point $x = x_0, v = 0$. The two branches lie on either side of the line $v = b$, and have both positive v for $x > x_0$, negative v for $x < x_0$. Neither of the branches touch the line $v = b$, but as follows from (2), both form an angle with it, which is the greater as n approaches closer to 1. This last result may be verified by a direct determination of the direction. For:

$$\begin{aligned}
 \left(\frac{dv}{dx}\right)_{\frac{dp}{dx}=0} &= \frac{\frac{d^2p}{dx^2}}{\frac{d^2p}{dv dx}} = \frac{\frac{2MRT}{(v-b)^3} \left(\frac{db}{dx}\right)^2 + \frac{MRT}{(v-b)^2} \frac{d^2b}{dx^2} - \frac{d^2a'}{v^2}}{\frac{2MRT db}{(v-b)^3 dx} - \frac{2}{v^3} \frac{da}{dx}} \\
 &= \frac{2MRT \left(\frac{db}{dx}\right)^2 - \frac{(v-b)^3}{v^3} \frac{d^2a}{dx^2} + MRT \frac{\frac{d^2b}{dx^2}}{\frac{db}{dx}} (v-b)}{2MRT \frac{db}{dx} - 2 \frac{da}{dx} \left(\frac{v-b}{v}\right)^3} \\
 &= \frac{\frac{db}{dx} \pm \frac{n v \sqrt{n}}{2MRT} \left(\frac{db}{dx}\right)^2 + \frac{1}{2} \frac{d^2b}{dx^2} (v-b)}{1 \pm \sqrt{n}} = \frac{\frac{db}{dx}}{1 \pm \sqrt{n}} \quad (3)
 \end{aligned}$$

because the second and the third member of the numerator vanish when we approach $v = 0$.

It is clear that $\frac{dp}{dx} = 0$ has again an asymptote for that value of x , for which $\frac{da}{dx} = MRT \frac{db}{dx}$, while no points of $\frac{dp}{dx} = 0$ are found on the leftside of $\frac{da}{dx} = 0$, at least as long as we are on the righthand side of the point $\frac{db}{dx} = 0$ on the supposition of a quadratic function for b .

Now too $\frac{dp}{dx} = 0$ will approach asymptotically to the line $v = b$ on the righthand side of the diagram, when we assume the linear form for b . If we accept the quadratic form for b , $\frac{dp}{dx} = 0$ approaches asymptotically to a line found from $v = b$ by multiplying all the coordinates by :

$$\frac{1}{1 + \frac{MRT (b_1 + b_2 - 2b_{12})}{a_1 + a_2 - 2a_{12}}}$$

From all these data follows the form for $\frac{dp}{dx} = 0$ indicated in fig. 1.

If we take the temperature higher, so that for $x = x_0$:

$$\frac{MRT \frac{db}{dx}}{\frac{da}{dx}} > 1$$

this shape is reduced to a shape which, as regards its realizable part, agrees perfectly with the ordinary one. For then there is an

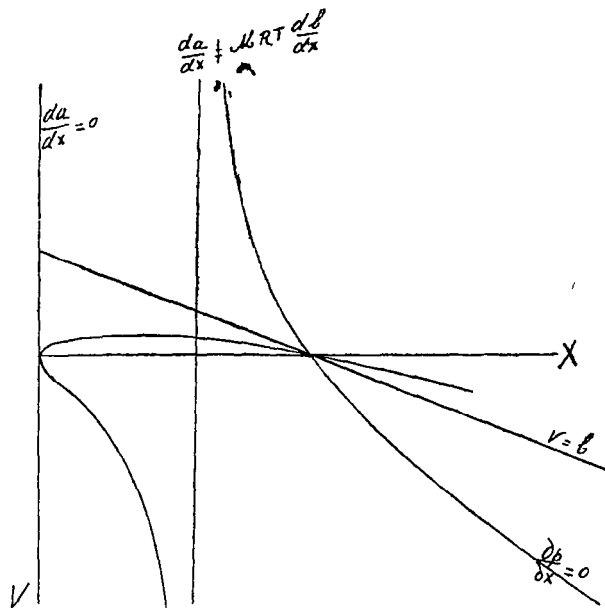


Fig. 1.

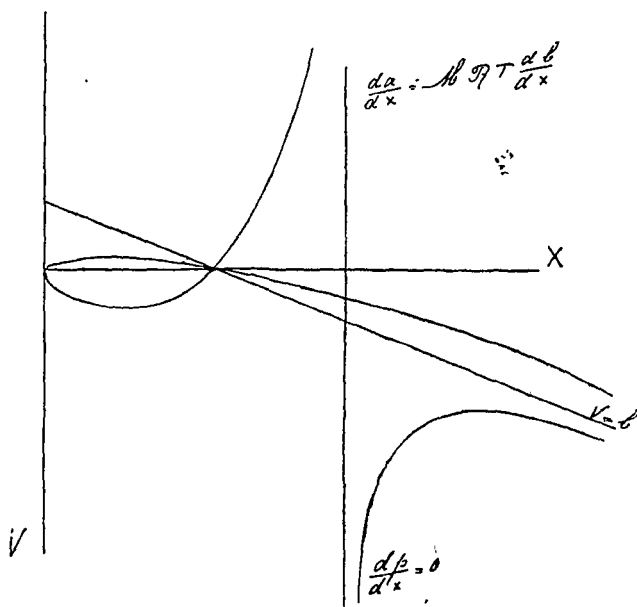


Fig. 2.

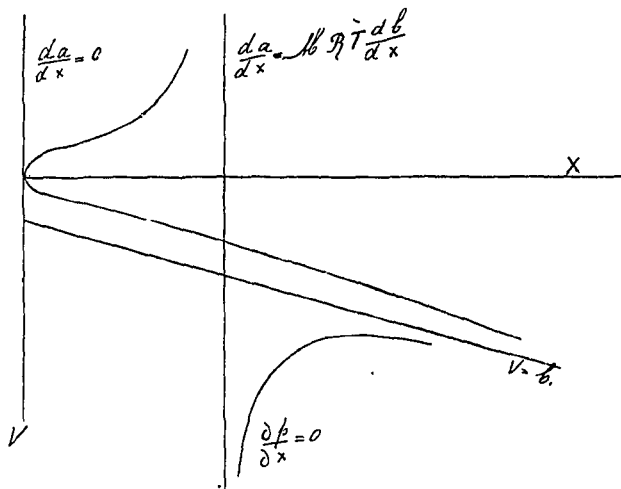


Fig. 3.

asymptote on the right of x_0 , viz. where $\frac{da}{dx} = MRT \frac{db}{dx}$. The course in the double point $x = x_0$, $v = 0$ now follows again from (2), provided it is borne in mind that now $n > 1$. (See fig. 2). For comparison we reproduce the complete diagram for the ordinary case in fig. 3, which will not require any elucidation. Only the transition temperature between fig. 1 and 2, for which $\frac{da}{dx} = MRT \frac{db}{dx}$ just at $x = x_0$, calls for discussion. To simplify the calculation we introduce as origin of the coordinates the point $x = x_0$, $v = 0$; in its neighbourhood we may put:

$$\frac{da}{dx} = MRT \frac{db}{dx} + MRT \frac{db}{dx} C_1 x$$

and

$$b = C_2 x$$

where

$$C_1 = \frac{\frac{d^2 a}{dx^2} \frac{db}{dx}}{MRT \frac{db}{dx}}$$

and

$$C_2 = \frac{db}{dx}$$

so that the equation for $\frac{dp}{dx} = 0$ becomes:

$$\left(\frac{v - C_2 x}{v} \right)^2 = \frac{1}{1 + C_1 x} = 1 - C_1 x$$

if we neglect the second powers, from which follows for the two roots:

$$1 - \frac{C_2 v}{v} = 1 - \frac{C_1 v}{2} \quad 1 - \frac{C_2 v}{v} = -1 + \frac{C_1 v}{2}$$

$$v_1 = \frac{2C_1}{C_1} = \frac{2MRT \left(\frac{db}{dv} \right)^2}{\frac{d^2 a}{dv^2}} \quad v_2 = \frac{C_2 v}{2} = \frac{1}{2} b.$$

So we have one finite root and one root equal to zero from which follows fig. 4 for the course of $\frac{dp}{dv} = 0$.

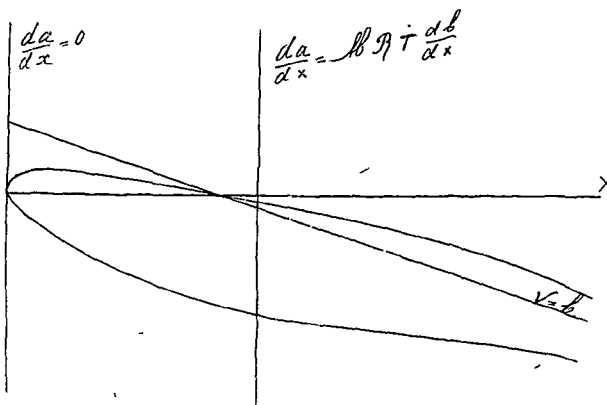


Fig. 4.

5. In the second place we have to examine the course of $\frac{dp}{dv} = 0$ in the case now under consideration. We may write the equation of this curve in the form:

$$MRT v^3 - 2a(v-b)^2 = 0.$$

It is very easy to separate the roots of this equation. For, when a is positive, the first member is negative for $v = 0$, positive for $v = b$, and positive for $v = \infty$. So there is a root between 0 and b , and either two or none for $v > b$, as is known, according as the critical temperature is below or above the critical temperature for the mixture under consideration. When b becomes equal to 0, both the product of the three roots and the sum of the products taken by twos becomes equal to zero. So there are two roots $v = 0$ in this case. And the third root assuming the value $\frac{2a}{MRT}$, the two branches

passing through the point $x = x_0$, $v = 0$, appear to be the liquid branch and the branch $v < b$, which has no physical signification. These two branches touch the line $v = b$ in the point mentioned as appears from the fact, that the product of these two roots is in the neighbourhood of this point b^2 , and the sum of these roots $2b$. Besides we can also prove this directly from the direction of the tangent. For:

$$\left(\frac{dv}{dx}\right)_{\frac{dp}{dv}=0} = -\frac{\frac{d^2p}{dv dx}}{\frac{d^2p}{dv^2}} = \frac{2MRT \frac{db}{dx} - \frac{2}{v^3} \frac{da}{dx}}{\frac{2MRT}{(v-b)^3} - \frac{6a}{v^4}}$$

If we substitute in this equation the value for $(v-b)$ from the equation for $\frac{dp}{dv} = 0$, we get:

$$\left(\frac{dv}{dx}\right)_{\frac{dp}{dv}=0} = \frac{2MRT \frac{db}{dx} - 2 \frac{\left(\frac{MRT}{2a}\right)^{3/2} v^{3/2}}{v^3}}{2MRT - \frac{6a \left(\frac{MRT}{2a}\right)^{3/2} v^{3/2}}{v^4}}$$

When we approach $v = 0$ the second members disappear in numerator and denominator, so that we keep:

$$\left[\left(\frac{dv}{dx}\right)_{\frac{dp}{dv}=0}\right]_{v=0} = \left[\frac{db}{dx}\right]_{b=0}$$

So for x little greater than x_0 , $\frac{dp}{dx} = 0$ will have greater volume than $\frac{dp}{dv} = 0$ for the same x . If, however, there should occur a minimum critical temperature in the system, and we shall see later on that this is very possible, there will be a point of intersection of $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$, which will, of course, constitute a fundamental point for the diagram of isobars.

Before proceeding to a discussion of the shape of the isobars themselves, we shall have to indicate for a complete elucidation of the problem discussed in the beginning, which gave rise to this inves-

tigation, in what way the lines $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$ get quite detached in this case. For this purpose we must ascertain what the relative position of these two curves will be at the temperature, at which $\frac{da}{dx} = MRT \frac{db}{dx}$ just for x_0 , and for which, therefore, fig. 4 holds. Now slightly on the right of x_0 , where b has very small values without a approaching to zero, the critical temperature is very high, so the two branches of $\frac{dp}{dv} = 0$ will certainly still exist on the right of x_0 . But this curve will be closed towards the righthand side, i.e. passing from x_0 to the right we shall first have mixtures which are below their critical temperature at the temperature considered, then mixtures which are already above it, and still further to the right we may sometimes meet with mixtures which are again below their critical temperature, sometimes not.

6. It is very easy to prove this on the supposition $b_{1,2} = \frac{1}{2}(b_1 + b_2)$. In this supposition we can give a very simple construction for the mixture with minimum critical temperature. Let the curve on which A lies (fig. 5) represent the values of a , the right line BD the

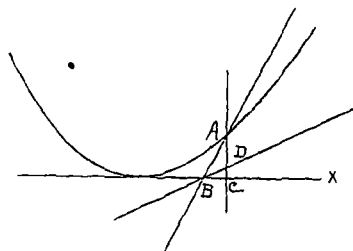


Fig. 5.

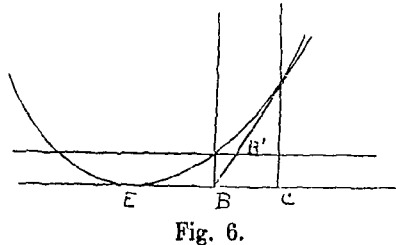


Fig. 6.

values of b , then :

$$\operatorname{tg} ABC = \frac{a}{b} \operatorname{tg} DBC$$

in the point A .

As $\operatorname{tg} DBC$ is constant, $\operatorname{tg} ABC$ is minimum if $\frac{a}{b}$ is minimum ; hence we find the mixture with minimum critical temperature by tracing a tangent to the curve from B . For this point of contact :

$$\left(\frac{da}{dx}\right)_C = \frac{27}{8} MRT_m \frac{db}{dx}$$

According to a well known property of the parabola the point B lies halfway between E and C , (fig. 6), and $\frac{da}{dx}$ being equal to zero in E , and increasing linearly with x :

$$\left(\frac{da}{dx}\right)_B = \frac{1}{2} \left(\frac{da}{dx}\right)_C = \frac{27}{16} MRT_m \frac{db}{dx}.$$

So for the asymptote of $\frac{dp}{dx} = 0$ to be found in B , so $\left(\frac{da}{dx}\right)_B = MRT \frac{db}{dx}$ we must raise the temperature to $\frac{27}{16} T_m$. A fortiori the thesis holds, of course, if, instead of $a_{1,2}^2 = a_1 a_2$, as was put here, $a_{1,2}^2 > a_1 a_2$. For instead of the combination of the curve with the right line EBC we get then the combination of the first-mentioned with the right line through B' , and B' lying to the right of B , the temperature will have to be raised still higher than just now, for $\frac{da}{dx}$ to be $= MRT \frac{db}{dx}$ in the point B' .

Also in the general case for b we can demonstrate the property mentioned, and it will appear afterwards that for these general considerations it is desirable not to replace the quadratic form of b unnecessarily by the linear one. We treat the case $a_{1,2}^2 > a_1 a_2$ at once, so that $a = 0$ has two real roots. We choose the point B' as origin; we call the abscissae of the points where $\frac{db}{dx} = 0$, $\frac{da}{dx} = 0$ and $a = 0$ in absolute value resp. x_1 , x_2 , x_3 , then we can write the equations for a and b (see fig. 7):

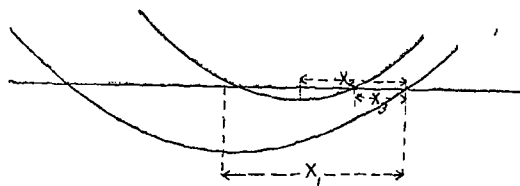


Fig. 7.

$$a = a_1 (x + x_2)^2 - a_1 (x_2 - x_3)^2 = a_1 (x^2 + 2x x_2 + 2x_2 x_3 - x_3^2)$$

$$b = b_1 (x + x_1)^2 - b_1 x_1^2 = b_1 x^2 + 2b_1 x_1 x$$

The temperature at which the asymptote of $\frac{dp}{dx} = 0$ reaches the point B' is determined by:

(610)

$$MRT = \left[\begin{array}{c} \frac{da}{dx} \\ \frac{db}{dx} \end{array} \right]_{x=0} = \frac{a_1 x_2}{b_1 x_1}.$$

Now we must investigate if there exist mixtures for which this temperature is the critical one on the right of B' . And so:

$$\frac{a_1 x_2}{b_1 x_1} = MRT = \frac{8}{27} \frac{a}{b} = \frac{8}{27} \frac{a_1 (x^2 + 2x x_2 + 2x_2 x_3 - x_3^2)}{b_1 (x^2 + 2x x_1)}.$$

So for the determination of x we find the equation:

$$x^2 \left(x_2 - \frac{8}{27} x_1 \right) + \frac{38}{27} x_1 x_2 x - \frac{8}{27} x_1 x_3 (2x_2 - x_3) = 0.$$

If for the sake of brevity we call the coefficient of x^2 A , the roots are:

$$x = -\frac{19}{27} \frac{x_1 x_2}{A} \pm \frac{1}{A} \sqrt{\frac{19^2}{27^2} x_1^2 x_2^2 + \frac{8}{27} A x_1 x_3 (2x_2 - x_3)}$$

If A is positive, the roots are real, as according to the supposition x_2 is $> x_3$, and the expression under the radical sign being larger than $\frac{19}{27} x_1 x_2$, we get a positive and a negative root. So this means that one mixture on the right of B' has its critical temperature at the said temperature. Hence the line $\frac{dp}{dv} = 0$ has a direction // v -axis at this x , and $\frac{dp}{dv} = 0$ does not exist any longer on the right of this mixture.

If A is negative, both roots remain real, for then we get under the radical sign:

$$\frac{19^2}{27^2} x_1^2 x_2^2 + \frac{8}{27} x_1 x_2 x_3 (2x_2 - x_3) - \frac{128}{27^2} x_1^2 x_2 x_3 + \frac{64}{27^2} x_1^2 x_3^2$$

As $x_2 > x_3$, the second term is positive, and the third is smaller than the first. So the expression under the radical sign is positive, but smaller than $\frac{19}{27} x_1 x_2$. The first term of the expression for the roots now being positive, we have now two positive values of x , i. e. on the left of B' we have first a region of mixtures which are below their critical temperature, then a region of mixtures which are already above it, and on this follows again a region of mixtures below their critical temperature. So the line

$\frac{dp}{dv} = 0$ has split up into two branches. We need not concern ourselves about the righthand branch at least now, for the detaching of $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$. For the point with minimum volume of this branch — which has the well-known shape — lies on the line $\frac{d^2p}{dvdx} = 0$, and so at greater volume than $\frac{dp}{dx} = 0$. The line $\frac{dp}{dx} = 0$ can, therefore, intersect this rightside part only in the branch of the two curves where $\frac{dv}{dx} > 0$, and this intersection does not offer anything noteworthy for our present investigation. So we have only to examine how $\frac{dp}{dx} = 0$ intersects the leftside half of $\frac{dp}{dv} = 0$ and detaches itself from this left side half or the only one that is left at this temperature in the case just discussed that A is positive.

7. Now we saw before that in fig. 4 the point where $\frac{dp}{dx} = 0$ intersects the line $x = x_0$, lies at a value of v :

$$v_1 = \frac{2 MRT \left(\frac{db}{dx} \right)^2}{\frac{d^2a}{da^2}}$$

At a temperature somewhat but very little lower, $\frac{dp}{dx} = 0$ will have nearly the same course on the right of $x = x_0$, as in fig. 4, then, very near the value $x = x_0$, $v = v_1$ it will abruptly turn upwards and pass through the point $x = x_0$, $v = 0$. This follows also from the coefficient of direction, which approaches ∞ according to formula (3). At somewhat higher temperature the first part will remain almost unchanged, but the curve, having got very near $x = x_0$, $v = v_1$ will now turn abruptly downward to an asymptote lying somewhat to the right of x_0 . So the question whether for this temperature a double intersection of $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$ will exist, which will necessarily lead to a contact afterwards, before the curves get quite

detached, is entirely dependent on the fact whether the point $x = x_0, v = v_1$ lies outside or inside $\frac{dp}{dv} = 0$ for the temperature considered, as appears clearly from the figs. 8 and 9. Now as we saw before the point where $\frac{dp}{dv} = 0$ intersects the line $x = x_0$ is determined by :

$$v_2 = \frac{2a}{MRT}$$

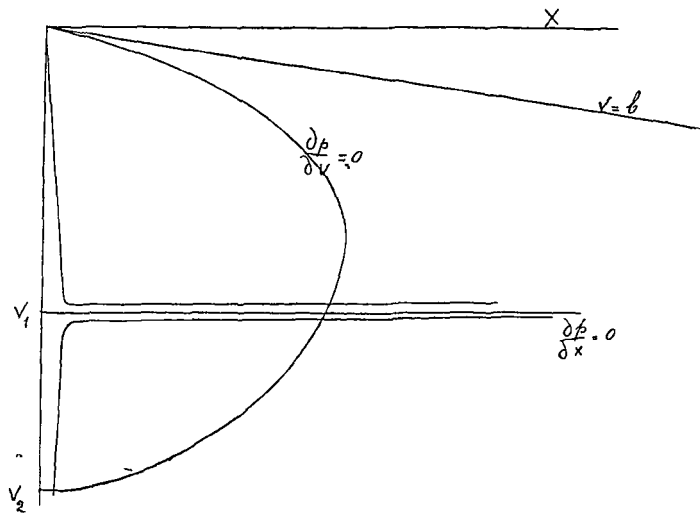


Fig. 8.

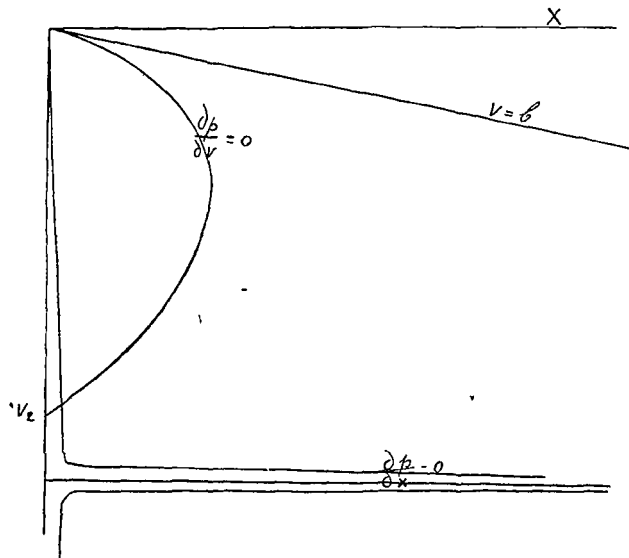


Fig. 9.

Accordingly the question whether for a temperature somewhat higher than that for which for $x_0 \frac{da}{dx} = MRT \frac{db}{dx}$, there will be double intersection and then contact, or no intersection of the two curves, will depend on the fact whether the expression .

$$\frac{v_1}{v_2} = \frac{\frac{2MRT \left(\frac{db}{dx}\right)^2}{\frac{d^2a}{dx^2}}}{\frac{2a}{MRT}}$$

or, since we have here $\frac{da}{dx} = MRT \frac{db}{dx}$:

$$\frac{v_1}{v_2} = \frac{\left(\frac{da}{dx}\right)^2}{a \frac{d^2a}{dx^2}} = \frac{2 \left(\frac{da}{dx}\right)^2}{4(a_1 a_2 - a^2_{12}) + \left(\frac{da}{dx}\right)^2}$$

will be smaller or larger than 1. So for the case $a_1 a_2 = a^2_{12}$ there is no longer any question of intersection above the temperature

$$MRT = \left[\frac{\frac{da}{dx}}{\frac{db}{dx}} \right]_{x=x_0}$$

because then v_1 is twice as large as v_2 , and a_{12} must have considerably descended below this value, before there can be question of this. Just as VAN DER WAALS derived (These Proc. June 1908) we get contact if $v_1 = v_2$, and so

$$\frac{\left(\frac{da}{dx}\right)^2}{a \frac{d^2a}{dx^2}} = 1.$$

It appears that the value of $\frac{b}{v}$, which belongs to the point of contact (loc. cit. fig. 32) becomes equal to zero in this case, not because the denominator becomes infinite, but because the numerator becomes zero.

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In a subsequent communication I hope to indicate the course of the isobars in the case given here, and to examine by the aid of a general survey of the possible combinations of a 's and b 's, whether besides the diagram of isobars given by VAN DER WAALS and the one treated here there are other diagrams of isobars possible for mixtures of normal substances with a 's and b 's which are quadratic functions of x .

ERRATUM.

p. 294 line 20 read $6|b a d c$, for $6|b c d a$.
„ 22 read $8|d c b a$, for $8|d a b c$.

(February 25, 1909).