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by a corresponding one in which the constant index i is given to the coefficients a, b, c , so we have:

$$G = \left[\frac{g_i^2}{g} (a_i \alpha + b_i \beta + c_i \gamma)^2 \right] = g_i (a_i \alpha + b_i \beta + c_i \gamma)$$

from which results after division by g_i^2 the relation I was to prove.

Using this relation I find:

$$M_h^2 = (1 - a_i \alpha - b_i \beta - c_i \gamma) \frac{\mu^2}{g_i}.$$

If we call $a \alpha + b \beta + c \gamma = x$, then $f \sqrt{\frac{g}{1-x}}$ can be calculated out of each apparent error and the mean value of this system of errors is equal to μ , as that of the system of unknown errors is $k \sqrt{g}$. It therefore seems to me not only permissible, but for a test of the weights even useful, to make use of that system of errors which allows the mean error of the unity of weight to be deduced out of each definite part of these errors. The connection between the quantities x and the number k of the above formula applied by me can be indicated by the relation $\Sigma x = k$.

Physics. - "Contribution to the theory of binary mixtures". VII.

By Prof. J. D. VAN DER WAALS.

ON THE RELATION BETWEEN THE QUANTITIES a_{12} AND a_1 AND a_2 , WHICH OCCUR IN THE THEORY OF A BINARY MIXTURE.

I have already frequently traced the course of the thermodynamic curves for the case that for a binary system minimum plaitpoint temperature occurs, and so also the quantity $\frac{a_x}{b_x}$ has a minimum value for certain value of x . Both the course of the isobars and the course of the lines $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$ may be assumed as known for that case. And experiment has shown that the shape of these lines predicted by theory it at least qualitatively accurate.

I purpose to demonstrate in these pages that in the case mentioned the course of these lines (see among others fig. 1 page 626 Vol. IX of these Proceedings 1907) is not compatible with the supposition $a_{12}^2 = a_1 a_2$.

I begin with pointing out that the line $\left(\frac{dp}{dx}\right)_v = 0$ has an asymptote for such a value of x for which $MRT \frac{db}{dx} = \frac{da}{dv}$, which asymptote either exists or must be supposed to exist for a value of x which is negative, and that this curve approaches the line $v = b$ asymptotically for continually increasing values of x — at least if $a_1 + a_2 - 2a_1$ is positive. I shall presently come back to this supposition, but on page 626 I have explicitly stated this supposition in the form $\frac{d^2a}{dx^2}$ positive. With increase of T this line proceeds to higher value of x and v .

At lower temperatures the line $\left(\frac{dp}{dv}\right)_x = 0$ consists of two separate branches. From $\frac{d^2p}{dv^2} \frac{dv}{dx} + \frac{d^2p}{dx dv} = 0$ follows that the liquid branch has maximum volume on the line $\frac{d^2p}{dx dv} = 0$ and the vapour branch minimum volume on the same curve, which curve has an analogous course to $\left(\frac{dp}{dx}\right)_v = 0$. It has the same asymptotes, but is always confined to greater volume. For $T =$ minimum critical temperature the two branches coincide in a point for which both $\frac{d^2p}{dv^2}$ and $\frac{d^2p}{dx dv}$ is equal to 0, so in such a point of the line $\frac{d^2p}{dx dv} = 0$, for which $\left(\frac{dp}{dv}\right)_x = 0$ and also $\frac{d^2p}{dv^2} = 0$. Hence in the critical point of the mixture taken as homogenous, for which $\frac{a_x}{b_x}$ has minimum value. At still higher value of T the curve $\left(\frac{dp}{dv}\right)_x = 0$ has split up into a lefthand branch and a righthand branch, both which branches possess tangents parallel to the v -axis, in points for which also $\left(\frac{dp}{dv}\right)_x = 0$ and $\frac{d^2p}{dv^2} = 0$. Among the special values of this constantly increasing value of T we must mention in the first place that for which the last mentioned point has got on the line $\left(\frac{dp}{dx}\right)_v = 0$, the point P of fig. 31. This is the

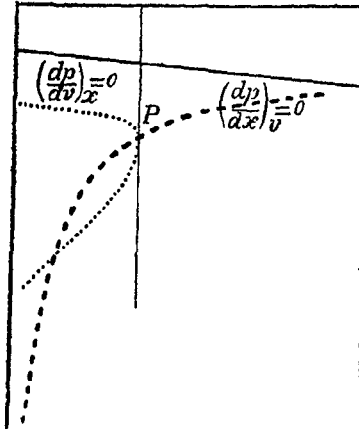


Fig. 31.

remarkable point for which *plaitpoint* and *critical point of the mixture* taken as homogeneous coincide. So at this temperature the two curves $\left(\frac{dp}{dv}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$ still intersect in two points. The other point of intersection lies, of course, at greater volume. With further rise of temperature the two curves contract further. The line $\left(\frac{dp}{dv}\right)_v = 0$ moves to the right and the line $\left(\frac{dp}{dv}\right)_x = 0$ to the left. At a certain temperature these two curves touch, and at still higher temperature they have got quite detached. This point of contact of the two curves lies, of course, on the vapour branch of $\left(\frac{dp}{dv}\right)_x = 0$, and so has a greater volume than the critical volume.

We can calculate the volume in case of contact. The condition of contact of $\left(\frac{dp}{dv}\right)_x = 0$ and $\left(\frac{dp}{dv}\right)_v = 0$ is given by equal value of $\frac{dv}{dx}$ in the two following equations:

$$\frac{d^2p}{dv^2} \frac{dv}{dx} + \frac{d^2p}{dx dv} = 0$$

and

$$\frac{d^2p}{dx dv} \frac{dv}{dx} + \frac{d^2p}{dx^2} = 0$$

or from:

$$\frac{d^2p}{dv^2} \frac{d^2p}{dx^2} = \left(\frac{d^2p}{dx dv}\right)^2 \quad (\text{see p. 691}).$$

This latter equation and the two equations $\left(\frac{dp}{dv}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$ form a set of three which is sufficient for the determination of the three quantities x , v and T of the point of contact. If we assume b to be constant in the equation of state these equations have the following form:

$$\left[\frac{MRT}{(v-b)^3} - \frac{3a}{v^4} \right] \left[\frac{MRT \left(\frac{db}{dx}\right)^2}{(v-b)^3} - \frac{1}{2} \frac{d^2a}{v^2} \right] = \left[\frac{MRT \frac{db}{dx}}{(v-b)^3} - \frac{da}{v^3} \right]^2 \quad \dots \quad (1)$$

$$\frac{MRT}{(v-b)^2} \frac{db}{dx} = \frac{da}{dx} \frac{1}{v^2} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (2)$$

and

$$\frac{MRT}{(v-b)^2} = \frac{2a}{v^3} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (3)$$

If now we make use of (2) and (3) for the elimination of MRT and of $\frac{db}{dx}$, we get a simple form for $\frac{v}{b}$, viz. :

$$\frac{v}{b} = \frac{3a \frac{d^2a}{dx^2} - 2 \left(\frac{da}{dx} \right)^2}{a \frac{d^2a}{dx^2} - \left(\frac{da}{dx} \right)^2} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (4)$$

We may also get a quadratic equation in $\frac{v}{b}$, but then it appears that one of the values of $\frac{v}{b} = 1$, and that at $T=0$ the line $v=b$ may be considered as coinciding with the branch of the volumes of $\left(\frac{dp}{dv} \right)_x = 0$, and also with $\left(\frac{dp}{dx} \right)_v = 0$. In the same way the line $v = \infty$.

If we now write for the ratio of $\left(\frac{da}{dx} \right)^2$ and $a \frac{d^2a}{dx^2}$ the quantity m , so that $m = \frac{\left(\frac{da}{dx} \right)^2}{a \frac{d^2a}{dx^2}}$ then (4) becomes :

$$\frac{v}{b} = \frac{3-2m}{1-m}.$$

And drawing $\frac{v}{b}$ as ordinate when m is laid out along the axis of the abscissae, we get fig. 32. For $m=0$ we have $\frac{v}{b} = 3$ and for $m=1$ we have $\frac{v}{b} = \infty$. For $m > 1$ $\frac{v}{b}$ is at first negative, but for $m = 3/2$, $\frac{v}{b} = 0$, and for greater values of m $\frac{v}{b}$ is positive and steadily increasing. The limiting value is $\frac{v}{b} = 2$. For negative value of m $\frac{v}{b}$ is always positive, descending from $\frac{v}{b} = 3$ to $\frac{v}{b} = 2$. The

traced curve is an equilateral hyperbola. So a value of $\frac{v}{b}$ larger than 3 is possible only when v lies between 0 and 1. Thus $\frac{v}{b} = 4$ requires a value of $m = 1/2$.

Accordingly it is impossible to account for a minimum plaitpoint temperature of substances for which m does not lie between 0 and 1.

Now I have already repeatedly called attention to the equation:

$$2a \frac{d^2a}{dx^2} = \left(\frac{da}{dx} \right)^2 + 4(a_1a_2 - a_{1,2}^2),$$

which follows from the supposition that a is a quadratic form of x , and already in my Molecular Theory for a binary mixture I pointed out, realizing the desirability of a relation being found between $a_{1,2}$ and a_1 and a_2 , that the equation of the spinodal line for a binary mixture might be very much simplified if we were justified in assuming $a_{1,2}^2 = a_1a_2$. I also pointed out other relations between these quantities; but I have carefully refrained from even giving so much as the slightest indication of the greater probability of one relation. I have only repeatedly, then and later, assumed as relation for mixtures with minimum plaitpoint temperature $a_1 + a_2 > 2a_{1,2}$, and reversely, when also mixtures with maximum plaitpoint temperature might occur: $a_1 + a_2 < 2a_{1,2}$. And I have repeatedly pointed out that there is no reason whatever for putting e. g. $a_{1,2}^2 = a_1a_2$. And to this the following considerations have chiefly led me.

In the equation of state for a simple substance the two constants b and a have not been introduced on equally sufficient grounds and with the same certainty. To the existence of the quantity b we conclude with perfect certainty if we believe that to occupy space is an essential property of matter. Even MAXWELL, who would not attribute a volume of their own to the molecules, but wanted to consider them as so-called material points, understanding that collisions could not take place between material points, could not but attribute to them at least an apparent volume. By assuming a repulsive force he had to account for their never meeting, and for their behaviour as particles possessing impermeability on approaching each other with reversal of motion. A hypothesis whose improbability is not to be denied. The force would be a repulsive one, and probably in inverse ratio to the fifth power of the distance. How and why the attraction at somewhat larger distance is converted into such a repulsive force is a question that was probably never put by him,

and at all events was not answered by him. So the introduction of the quantity b into the equation of state is perfectly natural — and for everybody who assumes the existence of matter as real, indispensable. But this is not, at least not in the same degree, the case with the quantity a . Why should molecular attraction be a necessary attribute of matter? From the idea: “matter is something that necessarily occupies space” does not follow that matter will also have to possess attraction. Perhaps we shall sooner or later learn to form a conception on the nature of a molecule which involves that they necessarily attract each other and learn to compute the value of this attraction. Of late attempts have therefore been made to get a better insight into the nature of molecules, and they are supposed to be either vibrating or permanent electrical double points¹⁾. But even if this supposition appeared to account satisfactorily for the molecular attraction, yet it does not necessarily follow that attraction exists. Then the question has changed in so far that it runs: are there electrical double points in the molecule or not? It is true that in my Thesis for the Doctorate (1873) p. 92, when the question occurred whether hydrogen possesses a critical temperature I answered in the sense of a high degree of probability, but only on a ground which leaves some room for doubt, viz. that “It may be presumed that matter will always have attraction”. It is not to be denied that everything that we accept as matter is subjected to gravity; but to derive from this that the existence of the NEWTONIAN attraction involves the possession of molecular attraction is more than hazardous. All this is not intended to raise doubt about the existence of a e. g. for helium, for now that all other substances possess a value for a we may repeat what I said before for hydrogen, but to draw attention to the fact that the value of a does not only depend on the molecular weight. If this *was* the case, $\frac{a_1}{m_1^2} = \frac{a_2}{m_2^2}$, a relation which is certainly not fulfilled. Then also $\frac{a_1}{m_1^2} = \frac{a_2}{m_2^2} = \frac{a_{12}}{m_1 m_2}$, and $a_{12}^2 = a_1 a_2$, which very probably will never be fulfilled either.

I was convinced from the outset that we should not be able to explain a number of phenomena occurring for binary mixtures by means of such an unfounded supposition. Already a long time ago KORTWEG showed in his paper “La surface ψ dans le cas de symétrie” in how high a degree the phenomena exhibited by a binary mixture, depend on the value ascribed to a_{12} . For values of a_{12} between

¹⁾ See these Proc. p. 132.

certain limits not only three phase equilibrium but even four phase equilibrium would be possible, then of course always at a single value of T . So the supposition $a_{1,2} = a_1 a_2$ is not one without far-reaching consequences. Yet we see repeatedly that this supposition is made. And I have undertaken this investigation to show that such a supposition would also render the existence of minimum plaitpoint temperature impossible. At the same time I wanted to point out how the course of the isobars which I have given in fig. 1 of these contributions would be entirely modified on other suppositions about $a_{1,2}$ than those I have started from. If we put in equation:

$$2a \frac{d^2 a}{dx^2} = \left(\frac{da}{dx} \right)^2 + 4 (a_1 a_2 - a_{1,2}^2)$$

for $\left(\frac{da}{dx} \right)^2$ the value $ma \frac{d^2 a}{dx^2}$ in which, if there is minimum plaitpoint temperature the value of m lies between 0 and 1 for the point of contact of $\left(\frac{dp}{dx} \right)_v = 0$ and $\left(\frac{dp}{dv} \right)_x = 0$, we find:

$$\left(\frac{2}{m} - 1 \right) \left(\frac{da}{dx} \right)^2 = 4 (a_1 a_2 - a_{1,2}^2)$$

$$(2 - m) a \frac{d^2 a}{dx^2} = 4 (a_1 a_2 - a_{1,2}^2)$$

Now $\frac{d^2 a}{dx^2} = 2(a_1 + a_2 - 2a_{1,2})$. As at the same time we cannot have $a_1 a_2 = a_{1,2}^2$ and $a_1 + a_2 = 2a_{1,2}$, unless in the case $a_1 = a_2$, this equation cannot be fulfilled but by putting $a_1 a_2 > a_{1,2}^2$.

The supposition $a_1 a_2 = a_{1,2}^2$ gives for m the value 2, but then also for $\frac{v}{b}$ in the point of contact of $\left(\frac{dp}{dx} \right)_v = 0$ and $\left(\frac{dp}{dv} \right)_x = 0$, the value 1 (see fig. 32). — Only when we put $a_1 a_2 < a_{1,2}^2$ does m become > 2 , and do we find for the point of contact of the curve mentioned, values of $\frac{v}{b}$ which are larger than 1, and which can therefore exist, but then this value can rise to 2 at the utmost. In such cases there is contact of $\left(\frac{dp}{dx} \right)_v = 0$ with the liquid branch of $\left(\frac{dp}{dv} \right)_x = 0$. And this means for fig. 1 of these contributions that then again the liquid branch of $\left(\frac{dp}{dv} \right)_x = 0$ may approach to $\left(\frac{dp}{dx} \right)_v = 0$ on the right side, but then to that part of this curve that lies beyond the minimum

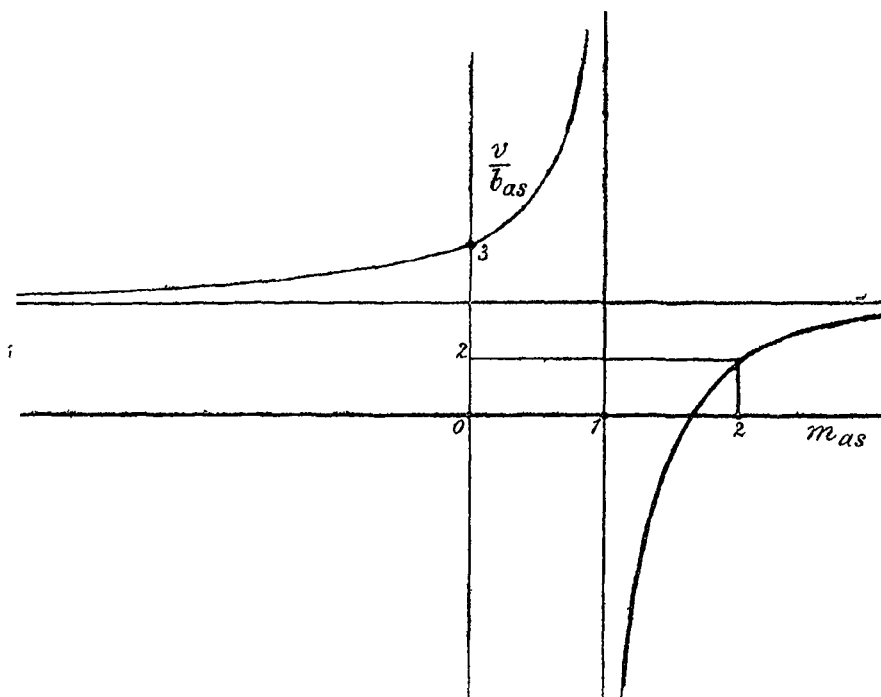


Fig. 32.

volume, and where it proceeds again to greater volumes. On the supposition that $a_1,^2$ might rise above $a_1 a_2$, fig. 1 would not represent all possible cases of the course of the isobars with respect to $\left(\frac{dp}{dx}\right)_v = 0$. But I observed already on page 630 in what way fig. 1 would have to be extended if other suppositions on $a_1 + a_2 - 2a_1$ are admitted e. g. $a_1 + a_2 - 2a_1 = 0$ or $a_1 + a_2 - 2a_1$ negative, and the supposition $a_1 a_2 < a_1^2$ lies in this direction.

If we continue increasing a_1 , not only above $\sqrt{a_1 a_2}$, but even above $\frac{a_1 + a_2}{2}$, then $m = \frac{\left(\frac{da}{dx}\right)}{a \frac{d^2a}{dx^2}}$ is negative, and $\frac{v}{b}$ lies between 2

and 3 for the point of contact of $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$, and so this point of contact always lies on the liquid branch of $\left(\frac{dp}{dv}\right)_x = 0$.

We might also have arrived at the above results by another course, which would give us an opportunity of making some new remarks. For if we think the quantity v eliminated from the two equations

$\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$, we obtain a relation between x and T . In general we find two values of x for the same value of T . The value of T , at which these values of x coincide, or in other words, the maximum value of T , then gives us the value of x for the point of contact of the two curves.

From

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

and

$$\frac{MRT}{(v-b)^2} \frac{db}{dx} = \frac{1}{v^2} \frac{dv}{dx}$$

we find

$$2 \frac{db}{dx} \frac{da}{dx} = \frac{da}{a} \frac{dv}{v} \text{ for a point of intersection. } \quad (6)$$

As for values of v which will be realisable, $v > b$ and v must be positive, a point of intersection of the two curves can only occur if

$\frac{da}{dx}$ is positive, and if $\frac{da}{a} < 2 \frac{db}{b} \frac{dx}{dx}$. This latter condition may be written

$\frac{d}{dv} \frac{a}{b^2} < 0$. So the two curves can never intersect in a region of increasing critical pressure. Let us therefore confine ourselves to decreasing critical pressure. The locus (6) has as differential equation:

$$- \frac{2 \frac{db}{dx} \frac{dv}{dx}}{v^2 \frac{dx}{dx}} = \frac{a \frac{d^2 a}{dx^2} - \left(\frac{da}{dx}\right)^2}{a^2} \quad (7)$$

So when $m = \frac{\left(\frac{da}{dx}\right)^2}{a \frac{d^2 a}{dx^2}} < 1$, $\frac{dv}{dx}$ is negative. Only in a region where

m has become $= 1$, $\frac{dv}{dx}$ will be positive. And if we should assume

$a_1 a_2 = a_{1,2}^2$, so if we put $m = 2$, the locus of the points of intersection of the two curves would move to greater volume with increasing x , so perfectly different from what happens for mixtures with minimum plaitpoint temperature. If we substitute the value of v which follows from (6), in:

$$MRT = \frac{2a}{b} \frac{b}{v} \left(1 - \frac{b}{v}\right)^2$$

we get:

$$MRT = \frac{a}{b} \frac{\frac{1}{a} \frac{da}{dx}}{\frac{1}{b} \frac{db}{dx}} \left\{ 1 - \frac{\frac{1}{2a} \frac{da}{dx}}{\frac{1}{b} \frac{db}{dx}} \right\}^2 \dots \dots \dots (7)$$

For values of x for which $\frac{da}{dx} = 0$ and $\frac{2}{b} \frac{db}{dx} = \frac{1}{a} \frac{da}{dx}$ or $\frac{d \log \frac{a}{b^2}}{dx} = 0$, the value of $T = 0$. Thus the same value of T always belongs to a couple of values of x which approach each other. And at the maximum value of T the two values of x have coincided. By differentiating (7) we get an equation which may be written in the form:

$$\frac{2a}{b} \frac{db}{dx} = \frac{3a \frac{d^2a}{dx^2} - 2 \left(\frac{da}{dx}\right)^2}{a \frac{d^2a}{dx^2} - \left(\frac{da}{dx}\right)^2} \frac{da}{dx}$$

from which, taking (6) into consideration, we obtain again (4).

It appears from the foregoing that putting $a_{12}^2 = a_1 a_2$ comes to the same thing as putting $m = 2$. For mixtures with minimum plait-point the value of m differs much from this value, as it is then smaller than 1, and so a_{12}^2 will have to differ pretty much from $a_1 a_2$. If we put $a_{12}^2 = l^2 a_1 a_2$, in which $l^2 < 1$, we find from:

$$2a \frac{d^2a}{dx^2} = \left(\frac{da}{dx}\right)^2 + 4(1-l^2) a_1 a_2$$

$$(2-m) a \frac{d^2a}{dx^2} = 4(1-l^2) a_1 a_2$$

or

$$\left(1 - \frac{m}{2}\right) (a_1 + a_2 - 2a_{12}) a = (1-l^2) a_1 a_2$$

It may be derived from this equation that m may lie near 2, even when l differs comparatively much from 1.

The value of a varying with x , also the ratio of $1 - \frac{m}{2}$ and $1-l^2$ will vary with x . If we make a increase with x , which probably will be in general the case, then a_1 is the smallest value of a and

a_2 , the greatest value, whereas the value of a for $x = \frac{1}{2}$ will be equal to $\frac{a_1 + a_2 + 2a_{12}}{4}$.

So the ratio $\frac{1 - \frac{m}{2}}{1 - l^2}$ is for $x = 0$, $x = \frac{1}{2}$ and $x = 1$:

$$\frac{1 - \frac{m}{2}}{1 - l^2} = \frac{a_2}{a_1 + a_2 - 2a_{12}} = \frac{\frac{a_2}{a_1}}{\left(\sqrt{\frac{a_2}{a_1} - 1}\right)^2 + 2(1-l)\sqrt{\frac{a_2}{a_1}}}$$

$$\frac{1 - \frac{m}{2}}{1 - l^2} = \frac{4a_1 a_2}{(a_1 + a_2)^2 - 4a_{12}^2} = \frac{4\frac{a_2}{a_1}}{\left(\frac{a_2}{a_1} - 1\right)^2 + 4(1-l^2)\frac{a_2}{a_1}}$$

$$\frac{1 - \frac{m}{2}}{1 - l^2} = \frac{a_1}{a_1 + a_2 - 2a_{12}} = \frac{1}{\left(\sqrt{\frac{a_2}{a_1} - 1}\right)^2 + 2(1-l)\sqrt{\frac{a_2}{a_1}}}$$

If we choose the second of these equations, from which it is easiest to draw conclusions with regard to the value of m at given value of l^2 , we write it first in the following form:

$$\frac{2}{m} - 1 = \frac{4(1-l^2)\frac{a_2}{a_1}}{\left(\frac{a_2}{a_1} - 1\right)^2}.$$

If we always take the same value of $1 - l^2$, but different values of $\frac{a_2}{a_1}$, we find very great differences in the value of m . For instance, with $\frac{a_2}{a_1} = 2$ we have $\frac{2}{m} - 1 = 8(1 - l^2)$, or $m = \frac{2}{1 + 8(1 - l^2)}$; but with $\frac{a_2}{a_1} = 11$, m is found equal to $m = \frac{2}{1 + 0,44(1 - l^2)}$. With $l^2 = 1$ we find of course in both cases $m = 2$. But for smaller values of l the values of m differ considerably. For $l = 0$ these values are $\frac{2}{9}$ and $\frac{2}{1,44}$.

If we had discussed the third of the equations, the values of m would have been found still higher. According to the first of the equations of course smaller.

Let us finally examine the course of the line $\left(\frac{dp}{dx}\right)_v = 0$ in the cases that there can be no contact with the line $\left(\frac{dp}{dv}\right)_x$, or only on the side of the liquid volumes. We saw already above, that then the locus of the points of intersection of the two curves mentioned (cf. 7) runs to greater volumes, if x is made to increase. Then at given T , only that part of the line $\left(\frac{dp}{dx}\right)_v = 0$ exists, for which this line runs to greater volume. The lefthand part, for which this curve may reach infinitely large volume lies in the common case at a value of x

to be calculated from $MRT \frac{db}{dx} = \frac{da}{dx}$. Then $\frac{v-b}{v} = \frac{MRT \frac{db}{dx}}{\frac{da}{dx}}$

and the first part of this equation is then equal to the unity, because $\frac{v}{b} = \infty$. But $\frac{v-b}{v}$ can also be equal to 1 in another case, viz.: if b should be $= 0$. This can only occur, when extrapolating we also admit negative values of x , and moreover choose for b such a function of x that it can become equal to 0 for negative value of x . This is the case for a linear function, but putting $b = b_1(1-x) + b_2x$ is only an approximation. Whether this can also be the case with a more exact shape of $b = f(x)$, must be left undecided. Moreover it is necessary, if we choose always greater negative value of x , that we first find $b = 0$, before finding $\frac{da}{dx} = 0$. But then the shape of the p -lines must also be modified. I shall however not enter into a discussion of this, for one reason because Dr. KOHNSTAMM informed me, that he had already been engaged in the study of the modified course of the isobars, and that he had also come to the conclusion that the relative situation of the values of x , for which $b = 0$ and $\frac{da}{dx} = 0$, is decisive. Moreover I leave undecided for the present whether also on other suppositions than $0 < x < 1$ there can be question of minimum plaitpoint temperature, which is to be distinguished from minimum value of $\frac{a_x}{b_x}$.