

Citation:

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Consequently, assuming the yearly motion to be constant, we find for the 14-monthly motion, both from the x and the y , values of the amplitude that decrease pretty regularly and pretty rapidly ¹⁾. For the epoch we find from the first and the second period a fairly good agreement ²⁾, whereas from the third we find a decidedly deviating value.

The reality of this last deviation is not very probable, and this tends to diminish the force of the arguments which are in favour of the acceptance of a decrease of the amplitude, which might be explained by frictional influences ³⁾.

Physics. — "*The properties of the pressure curves for co-existing phases of mixtures*". By Prof. J. D. VAN DER WAALS.

In the "Verslagen en Mededeelingen der Akademie voor 1891" I have deduced an explicite expression for the pressure in the case that one of the phases of a mixture may be considered as a rarefied gas.

Since that time the course of the value of the pressure for different mixtures has been determined experimentally in different ways, so that we are enabled to test the given formula at the results of the experiments.

In the given formula an auxiliary quantity μ_x occurs, which represents: $pv - \int p dv$ or $pv - MRT \log(v - b_x) - \frac{a_x}{v}$, while the differential coefficient of this quantity with respect to x , viz. $\left(\frac{d\mu_x}{dx}\right)_{p,T}$

may be approximately equated to $-\frac{d\frac{a_x}{b_x}}{dx}$.

As examples I draw attention to two shapes of these curves, which have been communicated in the Proceedings of this Academy: 1st. by Mr. HARTMAN for mixtures of CH_3Cl and CO_2 and 2nd by Mr. CUNAEUS for mixtures of Acetone and Ether. The curve traced by Mr. HARTMAN is remarkable on account of the simple shape of $p = f(x_1)$, which is almost a straight line, and that of Mr. CUNAEUS

¹⁾ See also *Archiv. Néerl.* T. II, p. 475 (29).

²⁾ See also *Archiv. Néerl.* T. II, p. 469 (23).

³⁾ CHANDLER finds by his empirical theory that the amplitude varies periodically and decreases in the years considered. It seems to me however that the foundation of his formula is not yet sufficiently certain.

on account of the fact, that in the curve $p = f(x_2)$ a distinct inflection point occurs.

The investigation in how far these curves agree with the given formula, will show that in one respect these two shapes may be considered as two limiting cases. For simplicity's sake I shall write henceforth μ_x instead of $\frac{\mu_x}{MRT}$. In the same way I shall represent

$\frac{\left(\frac{d\mu_x}{dx}\right)_{pT}}{MRT}$ by μ'_x , and a similar expression for the second differential coefficient by μ''_x . The value of these quantities for $x = 0$ and $x = 1$ will be: μ_0 , μ'_0 , μ''_0 and μ_1 , μ'_1 and μ''_1 . Then p may be represented by the formula:

$$p = MRT(1-x_1) e^{\mu_{x_1} - x_1 \mu'_{x_1} - 1} + MRT x_1 e^{\mu_{x_1} + (1-x_1) \mu'_{x_1} - 1}$$

or

$$p = p_0 (1-x_1) e^{\mu_{x_1} - \mu_0 - x_1 \mu'_{x_1}} + p_1 x_1 e^{\mu_{x_1} - \mu_1 + (1-x_1) \mu'_{x_1}}$$

In general we cannot express p explicitly as function of x_2 . But for the same value of p we have the following relation between x_1 and x_2 which may be derived from the equality of $\left(\frac{d\psi}{dx}\right)_{vT}$ for the two phases:

$$\frac{x_1}{1-x_1} e^{\mu'_{x_1}} = \frac{x_2}{1-x_2}.$$

If we take into consideration, that for very low temperatures,

the value of μ'_x is approximately equal to $-\frac{d \frac{a_x}{b_x}}{dx}$, we may indi-

cate a few limiting cases for the course of the quantities $\frac{a_x}{b_x}$, and the shapes which the pressure curves will assume in these limiting shapes. I have already assumed in my: "Théorie Moléculaire" that

by approximation μ'_x may be equated to $-\frac{d \frac{a_x}{b_x}}{dx}$ and the deductions which have there been obtained from this assumption, have since been confirmed to such an extent by the properties of the plaitpoint curves for mixtures, which show a minimum critical temperature,

that I feel justified in deriving further results from this approximation. I shall, however, first derive other equations which are independent of this approximation from the given values for p .

If we write $p = MRT e^{\mu_{x_1}} e^{-x_1 \mu'_{x_1}} \{1 - x_1 + x_1 e^{\mu'_{x_1}}\}$, then follows:

$$\begin{aligned} \frac{1}{p} \frac{dp}{dx_1} &= -x_1 \mu''_{x_1} + \frac{(e^{\mu'_{x_1}} - 1) + x_1 e^{\mu'_{x_1}} \mu''_{x_1}}{1 - x_1 + x_1 e^{\mu'_{x_1}}} = \\ &= \frac{(e^{\mu'_{x_1}} - 1) [1 + x_1 (1 - x_1) \mu''_{x_1}]}{1 - x_1 + x_1 e^{\mu'_{x_1}}}. \end{aligned}$$

This latter value agrees perfectly with that which is found by starting from the rigorously correct equation:

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

if compared with v_2 , the volume of a molecule in the vapour phasis, we neglect the value of v_1 and $\left(\frac{dv_1}{dx_1} \right)_{pT}$ and equate v_2 to $\frac{MRT}{p}$. We may namely put $\psi + pv$ for ζ ; we find then:

$$\left(\frac{d\zeta}{dx_1} \right)_{pT} = MRT \log \frac{x_1}{1 - x_1} + \left(\frac{d\mu}{dx_1} \right)_{pT}$$

and

$$\left(\frac{d^2 \zeta}{dx_1^2} \right)_{pT} = \frac{MRT}{x_1 (1 - x_1)} + \left(\frac{d^2 \mu}{dx_1^2} \right)_{pT}$$

After elimination of x_2 we find:

$$\frac{1}{p} \frac{dp}{dx_1} = \frac{x_2 - x_1}{x_1 (1 - x_1)} \left\{ 1 + x_1 (1 - x_1) \mu''_{x_1} \right\} = \frac{(e^{\mu'_{x_1}} - 1) [1 + x_1 (1 - x_1) \mu''_{x_1}]}{(1 - x_1) + x_1 e^{\mu'_{x_1}}}$$

The following wellknown facts may be deduced from this equation:

1st. $\frac{dp}{dx_1} = 0$ if $e^{\mu'_{x_1}} = 1$ or $\mu'_{x_1} = 0$ or $x_2 = x_1$ and 2nd $\frac{dp}{dx_1} = 0$ if

$1 + x_1 (1 - x_1) \mu''_{x_1} = 0$ or $\left(\frac{d^2 \zeta}{dx_1^2} \right)_{pT} = 0$.

From

$$\frac{dp}{dx_1} = p \frac{(e^{\mu'_{x_1}} - 1) [1 + x_1 (1 - x_1) \mu''_{x_1}]}{1 - x_1 + x_1 e^{\mu'_{x_1}}}$$

we deduce

$$\begin{aligned} \frac{\frac{d^2p}{dx_1^2}}{\frac{dp}{dx_1}} &= \frac{1}{p} \frac{dp}{dx_1} \frac{(e^{\mu'_{x_1}} - 1) + x_1 e^{\mu'_{x_1}} \mu''_{x_1}}{1 - x_1 + x_1 e^{\mu'_{x_1}}} + \frac{e^{\mu'_{x_1}} \mu''_{x_1}}{e^{\mu'_{x_1}} - 1} + \\ &\quad + \frac{(1 - 2x_1) \mu''_{x_1} + x_1 (1 - x_1) \mu'''_{x_1}}{1 + x_1 (1 - x_1) \mu''_{x_1}} \end{aligned}$$

or

$$\begin{aligned} \frac{\frac{d^2p}{dx_1^2}}{\frac{dp}{dx_1}} &= \mu''_{x_1} \left\{ -x_1 + \frac{e^{\mu'_{x_1}}}{e^{\mu'_{x_1}} - 1} + \frac{(1 - 2x_1)}{1 + x_1 (1 - x_1) \mu''_{x_1}} \right\} + \\ &\quad + \mu''_{x_1} \frac{x_1 (1 - x_1)}{1 + x_1 (1 - x_1) \mu''_{x_1}}. \end{aligned}$$

Let us put some special cases:

Put

$$e^{\mu'_{x_1}} = 1 \text{ or } \mu'_{x_1} = 0, \dots \dots \dots (a)$$

then:

$$\frac{d^2p}{dx_1^2} = p \mu''_{x_1} \{ 1 + x_1 (1 - x_1) \mu''_{x_1} \}$$

If μ''_{x_1} is positive, $\frac{d^2p}{dx_1^2}$ is also positive; so in this case there is a minimum pressure. But from the assumption that $MRT \mu'_{x_1}$ may

be equated with $-\frac{d\left(\frac{a_{x_1}}{b_{x_1}}\right)}{dx_1}$ follows: $MRT \mu''_{x_1} = -\frac{d^2\left(\frac{a_{x_1}}{b_{x_1}}\right)}{dx_1^2}$. We conclude therefore, that at very low T there is a minimum pressure for that mixture, for which $\frac{a_x}{b_x}$ has a maximum value. A mixture with a maximum value for $\frac{a_x}{b_x}$ has, however, not been found as yet, and it is even doubted whether this will ever occur for normal substances.

on $\left(\frac{a_1}{b_1^2} + \frac{a_2}{b_2^2} - 2\frac{a_{12}}{b_1 b_2}\right)$, so that all over the curve the sign remains invariable.

If on one of the sides the pressure should decrease, and if we put on that side $x_1 = 0$, then the value of $e^{\mu'_0}$ is smaller than 1. We get then $\frac{x_2}{x_1} < 1$. But not before $\frac{x_2}{x_1} < \frac{1}{2}$, the sign of $\left(\frac{d^2p}{dx_1^2}\right)_0$ will differ from that of μ''_0 .

If we have the exceptional case that there is a maximum pressure just on one of the sides then $e^{\mu'_0} = 1$, and therefore $\left(\frac{d^2p}{dx_1^2}\right) = p_1 \mu''_0$. This is almost, if not quite the case for the mixtures of acetone and ether investigated by Mr. CUNAEUS. On the ether-side the pressure is maximum, and the simple shape of the curve $p = f(x_1)$, for which the curvature is always such that $\frac{d^2p}{dx_1^2} < 0$, follows immediately from this supposition.

In this curve of CUNAEUS we have the case that one of the mixtures has a minimum critical temperature, though it is one of the components, but on the other hand in the curve of HARTMAN we have almost, if not quite the case, that μ'_x is constant for all values of x , and that there is therefore no question of a minimum critical temperature — not even if we should take x far beyond the limits of $x = 0$ and $x = 1$. It is not to be expected that this will ever be rigorously the case. Only if we put for b_x the approximate value $b_1(1-x) + b_2 x$, $\frac{a_x}{b_x}$ would be a linear function of x , in case

$\frac{a_1}{b_1^2} + \frac{a_2}{b_2^2} - 2\frac{a_{12}}{b_1 b_2}$ is equal to zero. But even if we do not introduce this approximate value of b_x , we may at least imagine as limiting case such a value of $\frac{a_x}{b_x}$, that it differs little from a straight line between 0 and 1. As limiting case we may therefore put $\mu'_x = \text{constant}$.

Then we get $\mu_{x_1} - x_1 \mu'_{x_1} = \mu_0$ and $\mu_{x_1} + (1-x) \mu'_{x_1} = \mu_1$, and

$$p = MRT(1-x_1) e^{\mu_0-1} + MRT x_1 e^{\mu_1-1}$$

or

$$p = p_0 (1-x_1) + p_1 x_1$$

Consequently $p = f(x_1)$ is exactly a straight line, which HARTMAN has found for mixtures of CO_2 and $\text{CH}_3 \text{Cl}$ by approximation.

Moreover, it follows immediately from the value which we have

found for $\frac{d^2p}{dx_1^2}$, that if we always put μ''_{x_1} and so also μ'''_{x_1} , as equal to zero, the value of this quantity is always equal to zero, and the pressure must be represented by a straight line.

In this special case it is also possible to give $p = f(x_2)$ explicitly. We have namely as relation between x_1 and x_2 :

$$\frac{x_2}{1-x_2} = \frac{x_1}{1-x_1} e^{\mu'_{x_1}} = \frac{x_1}{1-x_1} e^{\mu_1 - \mu_0} = \frac{x_1}{1-x_1} \frac{p_1}{p_0}$$

or

$$1-x_1 = \frac{1-x_2}{1-x_2 + \frac{p_0}{p_1} x_2}$$

and

$$x_1 = \frac{\frac{p_0}{p_1} x_2}{1-x_2 + \frac{p_0}{p_1} x_2}$$

Substituting these values we find:

$$p = \frac{p_0 p_1}{p_1 (1-x_2) + p_0 x_2}$$

The curve $p = f(x_2)$ traced by HARTMAN, resembles a hyperbola, but it deviates too much from it for the deviations to be ascribed to experimental errors. But in reality, these observations have been made at a too high temperature for considering the vapour phasis as a rarefied gasphasis. Specially for carbonic acid, where the pressure was even greater than 45 atmospheres, the deviations, caused by it, must have been considerable. It would be interesting to investigate whether at a lower temperature (HARTMAN observed at 9°, 5) the vapourbranch would approach closer to a hyperbola.

We may in this case write for $p = f(x_2)$:

$$\frac{1}{p} = \frac{1-x_2}{p_0} + \frac{x_2}{p_1},$$

from which, as we are here concerned with gasphases, follows:

$$v = v_0 (1-x_2) + v_1 x_2.$$

If we take therefore an arbitrary quantity of the saturated vapour

of the first substance, and also an arbitrary quantity of the saturated vapour of the second, and if they mix in a volume which is the sum of the two volumes, the mixture is again saturated vapour. This result deviates altogether from the law of DALTON applied to saturated vapour. But this law of DALTON will only hold good as an approximation, if the liquid, which would be formed through condensation, may be considered as unmixed liquid.

It is well-known that DANIEL BERTHELOT has put $a_{12}^2 = a_1 a_2$. I have refuted this opinion some time ago, first because the ground which was alleged for concluding to this relation, seemed incorrect to me, as it does still, but secondly because the great variety, which the critical phenomena of mixtures show, seemed to me to clash with the assumption of such a simple relation between a_{12} , a_1 and a_2 . Since I have learned to ascribe many complications, which mixtures show, to the anomaly of the components themselves, a great many objections, which I had against the relation $a_{12} = \sqrt{a_1 a_2}$, have lost their weight, and any rate I think it desirable to keep in view at every phenomenon the possibility, that this relation should be fulfilled. If we do so also in this case, the condition that $\frac{a_x}{b_x}$ be a linear function of x_1 , becomes at least by approximation the following:

$$\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right)^2 = 0$$

or the critical expressions of the components are the same. Now it is indeed remarkable, that in the mixture of HARTMAN, for which the critical temperatures are almost in the proportion of 3 to 4, the critical expressions differ comparatively little — that of CO_2 being equal to 73 and that of CH_3Cl to 65 or 66 atmospheres. The condition that the critical expressions must be the same for the components, is fulfilled if $T_{c_2} = T_{c_1} \frac{b_2}{b_1}$, so if the critical temperatures are proportional to the volumes of the molecules. And though this condition is not quite fulfilled for CO_2 and CH_3Cl , yet it is fulfilled in an incomparably greater degree than for the other examined mixtures, for which the substance with the smallest molecule possesses the highest critical temperature. So is in a mixture of acetone and ether the critical temperature of ether lower than that of acetone, whereas the volume of the molecules of ether exceeds that of acetone.

For acetone and ether the condition $\frac{\sqrt{a_1}}{b_1} = \frac{\sqrt{a_2}}{b_2}$ is certainly not ful-

filled and in close connection with this is the great difference in the curve determined by CUNAEUS as compared with that of HARTMAN ¹⁾.

In what precedes we have been specially occupied with the difference in the course of $p = f(x_1)$ for these mixtures. Let us also pay attention to $p = f(x_2)$. As the elimination of x_1 from the equation:

$$\frac{x_1}{1-x_1} e^{\mu'_{x_1}} = \frac{x_2}{1-x_2}$$

is not possible, when μ'_{x_1} depends on x_1 , p can generally not be expressed explicitly in x_2 . Yet we may deduce formulae for $\frac{dp}{dx_2}$ and $\frac{d^2p}{dx_2^2}$, which are of importance for the determination of the different shapes of these curves.

From the two strictly accurate equations:

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

and

$$v_{12} dp = (x_1 - x_2) \left(\frac{d^2\zeta}{dx_2^2} \right)_{pT} dx_2$$

follows, in case the second phasis is a rarefied vapour-phasis, and we may consequently put $v_{21} = v_2$ and $v_{12} = -v_2$:

$$\left(\frac{d^2\zeta}{dx_1^2} \right)_{pT} dx_1 = \left(\frac{d^2\zeta}{dx_2^2} \right)_{pT} dx_2$$

or

$$\frac{dx_1}{x_1(1-x_1)} \left\{ 1 + x_1(1-x_1) \mu''_{x_1} \right\} = \frac{dx_2}{x_2(1-x_2)}.$$

When the second phasis follows the gas laws sufficiently, the second term is simplified to the form given here.

By means of this relation between dx_1 and dx_2 and of the relation

$$\frac{x_2}{1-x_2} = \frac{x_1}{1-x_1} e^{\mu'_{x_1}}, \text{ we find:}$$

¹⁾ The value of a_{12} calculated by M₁. QUINT for mixtures of Cl H and C₂ H₆, however, does not fulfil the relation $a_{12} = \sqrt{a_1 a_2}$.

$$\frac{1}{p} \frac{dp}{dx_2} = \frac{1}{p} \frac{dp}{dx_1} \frac{dx_1}{dx_2} = \left(1 - e^{-\mu' x_1}\right) \left(1 - x_1 + x_1 e^{\mu' x_1}\right)$$

or

$$\frac{dp}{dx_2} = p \left(1 - e^{-\mu' x_1}\right) \left(1 - x_1 + x_1 e^{\mu' x_1}\right)$$

It appears from this formula that p as function of x_2 presents a maximum or a minimum only when $e^{\mu' x_1} = 1$. In the case, that a longitudinal plait exists, there are two more values of x_1 , for which p as function of x_1 might become maximum or minimum in the unstable region, but this is not the case for p as function of x_2 . The curve $p = f(x_2)$ presents two cusps for the values of x_2 , which are conjugated to those values of x_1 , for which $1 + x_1(1 - x_1) \mu''_{x_1}$ should be zero. This I have already pointed out in the *Théor. Mol.*

In order to determine $\frac{d^2 p}{dx_2^2}$ we differentiate the logarithm of the last equation, which yields:

$$\frac{\frac{d^2 p}{dx_2^2}}{\frac{dp}{dx_2}} = \frac{dx_1}{dx_2} \left\{ \frac{1}{p} \frac{dp}{dx_1} + \frac{(e^{\mu' x_1} - 1) + x_1 e^{\mu' x_1} \mu''_{x_1}}{1 - x_1 + x_1 e^{\mu' x_1}} + \frac{e^{-\mu' x_1} \mu'_{x_1}}{1 - e^{-\mu' x_1}} \right\}$$

or

$$\frac{d^2 p}{dx_2^2} = \frac{dp}{dx_2} \frac{dx_1}{dx_2} \left\{ \frac{2(e^{\mu' x_1} - 1)}{1 - x_1 + x_1 e^{\mu' x_1}} + \mu'_{x_1} \left[\frac{2x_1 e^{\mu' x_1}}{1 - x_1 + x_1 e^{\mu' x_1}} - x_1 + \frac{1}{e^{\mu' x_1} - 1} \right] \right\}$$

Special cases are:

(a) Be $1 + x_1(1 - x_1) \mu''_{x_1} = 0$, then $\frac{d^2 p}{dx_2^2} = \infty$, as $\frac{dx_1}{dx_2}$ is ∞ in this case. We have already pointed out, that the curve $p = f(x_2)$ presents cusps in the points conjugated to these values of x_1 .

(b) Be $\mu'_{x_1} = 0$, then $\frac{d^2 p}{dx_2^2} = p \frac{\mu''_{x_1}}{1 + x_1(1 - x_1) \mu''_{x_1}}$. If we compare this value with $\frac{d^2 p}{dx_1^2}$, it appears, that at the point of contact the two curves $p = f(x_1)$ and $p = f(x_2)$ lie on the same side of the tangent. The curvatures however are unequal, except in the case, that for such a point $x_1 = 0$. For the mixture of acetone and ether

this exception occurs at least approximately on the side of the ether.

$$(c) \text{ Be } x_1 = 0, \text{ then } \left(\frac{d^2 p}{dx_2^2} \right)_0 = p_0 \frac{2(e^{\mu'_0} - 1)^2 + \mu''_0}{(e^{\mu'_0})^2}.$$

This equation shows, that $\left(\frac{d^2 p}{dx_2^2} \right)_0$ will be negative only by exception; only when μ''_0 is negative and has a numeric value, greater than $(e^{\mu'_0} - 1)^2$. It may however occur, and that on both sides for mixtures with maximum-pressure. In the following three figures the curves $p = f(x_1)$ and $p = f(x_2)$, which may then occur, are drawn.

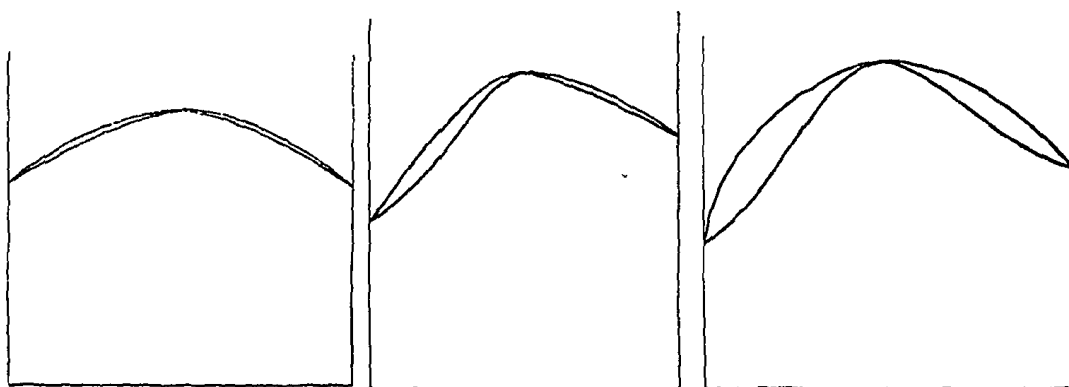


Fig. 1.

Fig. 2.

Fig. 3.

In fig. 1 a curve has been drawn, for which the maximum-pressure is not much greater than the pressures on both sides, and for which therefore $e^{\mu'_0} - 1$ has a small value, even on the sides. As in the case of a maximum-pressure the quantity μ'' is negative, $\left(\frac{d^2 p}{dx_2^2} \right)_0$ may be negative on both sides.

In fig. 2 this is the case only on one side, while in fig. 3 the value of $(e^{\mu'_0} - 1)$ is supposed to be great enough, to cause $\frac{d^2 p}{dx_2^2}$ to be positive on both sides.

The curve, traced by Mr. CUNAEUS relating to his investigation on acetone and ether is therefore to be considered as either the lefthand or the righthand half of fig. 3, and the point of inflection, which he has found, was to be expected, as on the side of acetone the value of $e^{\mu'_0} - 1 = \left(\frac{x_2 - x_1}{x_1} \right)_0$ is rather great, viz. 3,5.

From the value of x_1 and x_2 , at which the point of inflection has been found, we may derive the value of μ''_{x_1} with the aid of the

formula we have found for $\frac{d^2p}{dx_2^2}$. To that purpose we have to equate the factor of $\frac{dp}{dx_2} \frac{dx_1}{dx_2}$ to zero. If we substitute $\frac{x^2}{1-x_2} \frac{1-x_1}{x_1}$ for $e^{u''x_1}$, we may write this factor as follows :

$$\frac{1}{x_2 - x_1} \left\{ 2 \frac{(x_2 - x_1)^2}{x_1 (1 - x_1)} + \mu''_{x_1} \left[2 (x_2 - x_1)^2 + x_1 (1 - x_1) \right] \right\},$$

From this we deduce for the point of inflection :

$$-\mu'_{x_1} = \frac{2 \frac{(x_2 - x_1)^2}{x_1 (1 - x_1)}}{2 (x_2 - x_1)^2 + x_1 (1 - x_1)}$$

In the experiments of Mr. CUNAEUS, we are not perfectly sure of the values of x_1 and x_2 for the point of inflection¹⁾. The numeric value of μ''_{x_1} cannot therefore be found with accuracy. Put

$x_1 = \frac{1}{2}$ and $x_2 = \frac{2}{3}$, then the value of $-\mu'_{x_1} = \frac{8}{11}$, put $x_1 = 0,45$ and $x_2 = 0,65$, then the value of $-\mu'_{x_1}$, will be found slightly less than unity.

We can predict the course of the critical curves for mixtures of acetone and ether, from the properties of the pressure-curves for these mixtures at low temperatures. Let us imagine the critical curve, either the plaitpoint-curve or the curve of the critical points of contact of Cl H and $\text{C}_2 \text{H}_6$, and let us take the upper half of it, i.e. that part, that lies above the minimum-temperature. That minimum temperature, the critical point of ether, will be the starting point. We have therefore reason to expect that mixtures of ether in which a little quantity of acetone has been solved, will present r. c. II. But for these critical curves also it is to be expected that they will deviate so slightly from one another, that it will be difficult to observe the retrograde condensation²⁾.

¹⁾ In the determination of the vapour-phases by means of the refractive power, the circumstance, that the glass plates are covered with a condensed layer has an influence, which is probably large enough, to vitiate noticeably the values found for x_2 .

²⁾ Let us avail ourselves of this occasion to point out that the rule, given by Prof. KUENEN, to find r. c. II is not quite correct. Prof. KUENEN thought that r. c. II is to be looked for in mixtures of substances, of which that one, which has the highest critical temperature, has at equal temperatures also the highest vapour tensions. If we consider a plaitpoint curve, beginning exactly at the minimum critical temperature and therefore just beginning with r. c. II, the vapour tension of the component with the highest T_c will be lower than that of the other component; and the more so, when the difference between T_{c2} and T_{c1} is large.

Let us write the value of $\frac{d^2p}{dx_2^2}$ also under the following form:

$$\frac{d^2p}{dx_2^2} = p \left[\frac{x_1(1-x_1)}{x_2(1-x_2)} \right]^2 \left\{ 2 \left[\frac{(x_2-x_1)}{x_1(1-x_1)} \right]^2 + \frac{\mu''_{x_1}}{1+x_1(1-x_1)\mu''_{x_1}} \right\}.$$

This form enables us to conclude to the curvature of the vapour-branch, if it has an unstable part ¹⁾, in consequence of the presence of a longitudinal plait, which intersects the liquid branch. For this unstable part we have $1+x_1(1-x_1)\mu''_{x_1} < 0$, and μ''_{x_1} and $1+x_1(1-x_1)\mu'_{x_1}$ has the same sign. For this unstable part of the vapour branch we get therefore $\frac{d^2p}{dx_2^2} > 0$. Let us imagine two values of x_1 , differing very little from that which makes $1+x_1(1-x_1)\mu''_{x_1} = 0$, and chosen on either side of it, then $1+x_1(1-x_1)\mu''_{x_1}$ has either a very small positive value or a very small negative one, and therefore

$\frac{\mu''_{x_1}}{1+x_1(1-x_1)\mu''_{x_1}}$ a very great positive or a very great negative

value. This makes us conclude that the sign of $\frac{d^2p}{dx_2^2}$ changes for those values of x_2 , which are conjugated to these, at which the liquid branch enters or leaves the unstable region. At the extremities of the unstable part of the vapour branch we find therefore cusps. Consequently the two stable parts of the vapour-branch end with a negative value of $\frac{d^2p}{dx_2^2}$. As a rule the vapour-branch at $x=0$ and $x=1$ has a positive value of $\frac{d^2p}{dx_2^2}$, therefore there are also as a rule

two points, where $\frac{d^2p}{dx_2^2}$ will be equal to zero. Probably these points always lie near the cusps. The following figure gives a shape of the vapour branch fulfilling these conditions.

If before its end the vapour branch should possess a maximum, the second inflection point is unnecessary and its shape will be represented by fig. 5.

¹⁾ We use here the term "unstable part" to indicate that the phases, represented by it, could only co-exist with unstable phases. Considered in themselves these phases are stable.

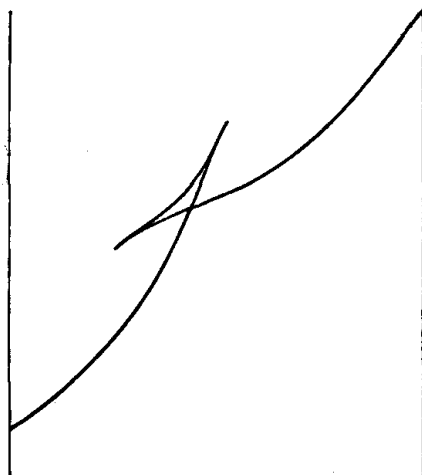


Fig. 4.

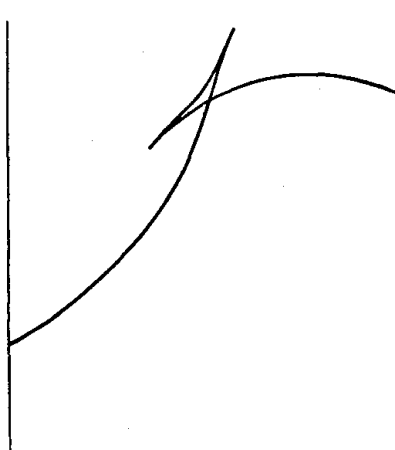


Fig. 5.

This latter figure represents the vapour branch of mixtures of phenol and water below the critical temperature of complete mixture.

If the second phasis is a rarefied gasphasis, the pressure of which is p , $p(1-x_2)$ represents the partial pressure of the first component and px_2 that of the second component. The value of these quantities is given by

$$p(1-x_2) = MRT(1-x_1) e^{\frac{\mu_{x_1} - x_1 \mu'_{x_1}}{T} - 1}$$

and

$$px_2 = MRT x_1 e^{\frac{\mu_{x_1} + (1-x_1) \mu'_{x_1}}{T} - 1}$$

and

$$p(1-x_1) = p_0(1-x_1) e^{\frac{\mu_{x_1} - \mu_0 - x_1 \mu'_{x_1}}{T}}$$

and

$$px_2 = p_1 x_1 e^{\frac{\mu_{x_1} - \mu_1 + (1-x_1) \mu'_{x_1}}{T}}$$

We conclude from this:

$$\frac{dp(1-x_2)}{dx_1} = -p \frac{1-x_2}{1-x_2} \left\{ 1 + x_1 (1-x_2) \mu''_{x_1} \right\}$$

$$\frac{dp x_2}{dx_1} = p \frac{x_2}{x_1} \left\{ 1 + x_1 (1-x_1) \mu''_{x_1} \right\}$$

and

$$\frac{d^2 p(1-x_2)}{dx_1^2} = p \frac{1-x_2}{1-x_1} \left\{ x_1 \mu''_{x_1} \left[1 + x_1 (1-x_1) \mu''_{x_1} \right] - \frac{d \left[1 + x_1 (1-x_1) \mu''_{x_1} \right]}{dx_1} \right\}$$

$$\frac{d^2 p x_2}{dx_1^2} = p \frac{x_2}{x_1} \left\{ (1-x_1) \mu''_{x_1} \left[1 + x_1 (1-x_1) \mu''_{x_1} \right] + \right. \\ \left. + \frac{d \left[1 + x_1 (1-x_1) \mu''_{x_1} \right]}{dx_1} \right\}$$

By adding the two last conditions, we find:

$$\frac{1}{p} \frac{d^2 p}{dx_1^2} = \mu''_{x_1} \left\{ 1 + x_1 (1-x_1) \mu''_{x_1} \right\} \left\{ \frac{x_2 (1-x_2)}{x_1 (1-x_1)} + \frac{(x_2-x_1)^2}{x_1 (1-x_1)} \right\} + \\ + \frac{x_2-x_1}{x_1 (1-x_1)} \frac{d \left\{ 1 + x_1 (1-x_1) \mu''_{x_1} \right\}}{dx_1},$$

a form to which we may also reduce the form given before. From the value for the first differential coefficients we deduce, that for substances, which are perfectly miscible, the partial pressure of one component decreases, when the second component is substituted for a part of it. From this follows that the total pressure must be smaller than the sum of the tensions of the separate components. If $1+x_1(1-x_1)\mu_{x_1}$ should be negative, the partial pressure of a component increases on the other hand by substitution by the second component. Then it will be the question whether the partial pressure cannot rise so high, that it exceeds the initial value.

This question, however, cannot be solved without the knowledge of the properties of the function μ .

Physics. — Dr. E. VAN EVERDINGEN JR.: "*The HALL-effect and the increase of resistance of bismuth in the magnetic field at very low temperatures.*" II. (Communication N^o. 58 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES).

1. From the measurements of the HALL-effect in bismuth at the boiling-point of liquid nitrous oxide and liquid oxygen, described in the Proceedings of 29 October 1899, p. 221 and 30 December 1899, p. 380, it appeared that the HALL-coefficient increased considerably with falling temperatures; it hence seemed desirable to determine this increase with greater accuracy. The measurements in liquid nitrous oxide had shown that the strength of the magnetic field had