

Citation:

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opinion are older (e. g. *C. nodiflora* FORST. and *C. sumatrana* JUNGH.) still survive for instance, in Australia, in Sumatra, Borneo, Celebes, and in the Moluccas, but recent forms are now wanting in Java, and fossil ones have not yet been found in Java.

5. Of the two Javanese indigenous species of *Casuarina*, *C. montana* JUNGH. appear to be phylogenetically younger than *C. equisetifolia* FORST.; the former species is probably a mutant, which has only maintained itself within the region of the Malay Archipelago, and which has arisen from the latter species.

6. Probably *C. montana* var. *validior* MIQ. is a mutant, which has maintained itself in Java only and which has arisen from *C. montana* var. *tenuior* MIQ.

Physics. — “Contribution to the theory of binary mixtures,” XI.

(Continued). By Prof. J. D. VAN DER WAALS.

Now we shall proceed to the investigation of some properties of the loci of the points of intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$, in the first place when this locus is a closed figure, lying wholly at volumes larger than b . Let us write.

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

in the form:

$$v^2 \left\{ 1 - x(1 - x) \frac{c}{a} \right\} - 2vb + \left\{ b_1^2 + x(b_2^2 - b_1^2) \right\} = 0. \quad (\varphi)$$

The form of the third term in this equation appears only to depend on the first power of x , because $b^2 + x(1 - x) \left(\frac{db}{dx} \right)^2$ may be written $b_1^2 + 2xb_1 \frac{db}{dx} + x^2 \left(\frac{db}{dx} \right)^2$ and to this added $x(1 - x) \left(\frac{db}{dx} \right)^2$. The third term then becomes $b_1^2 + \frac{db}{dx} \left(2b_1 + \frac{db}{dx} \right) x$, in which $\frac{db}{dx} = b_2 - b_1$.

If we put $x(1 - x) \frac{c}{a} = A$, the equation (φ) becomes

$$v^2(1 - A) - 2vb + b_1^2 + x(b_2^2 - b_1^2) = 0 \quad \dots (\varphi')$$

Let us seek the points of this line in which the tangent is parallel to the x -axis, and so in which $\frac{dv}{dx} = 0$; then we find another equation

by differentiating φ' with respect to x , and by keeping v constant, viz.:

$$-v^2 \frac{dA}{dx} - 2v(b_2 - b_1) + b_2^2 - b_1^2 = 0 \dots (\varphi'')$$

By eliminating v from (φ') and (φ'') , we obtain an equation in x only — and for the values of x which satisfy this resulting equation, $\frac{dv}{dx}$ will be $= 0$. We shall, however, seek a resulting equation in x in a somewhat different way.

If we subtract $x(\varphi'')$ from (φ') , we get:

$$v^2 \left\{ 1 - A + x \frac{dA}{dx} \right\} - 2vb_1 + b_1^2 = 0,$$

and adding this last equation to (φ'') , we get:

$$v^2 \left\{ 1 - A - (1 - x) \frac{dA}{dx} \right\} - 2vb_2 + b_2^2 = 0.$$

Hence:

$$\frac{b_1}{v} = 1 \pm \sqrt{A - x \frac{dA}{dx}}$$

and

$$\frac{b_2}{v} = 1 \pm \sqrt{A + (1 - x) \frac{dA}{dx}}.$$

Now $\frac{b_1}{v}$ is certainly smaller than 1, hence in the expression for $\frac{b_1}{v}$ only the sign — can be retained before the radical sign. And leaving undecided for the present whether $v > b_2$ or $v < b_2$, we find when we divide $\frac{b_2}{v}$ by $\frac{b_1}{v}$:

$$n = \frac{1 \pm \sqrt{A + (1 - x) \frac{dA}{dx}}}{1 - \sqrt{A - x \frac{dA}{dx}}}$$

or

$$n - 1 - n \sqrt{A - x \frac{dA}{dx}} \mp \sqrt{A + (1 - x) \frac{dA}{dx}} = 0. \quad (\varphi''')$$

Now

$$A + (1 - x) \frac{dA}{dx} = (1 - x)^2 \frac{c}{a} \left\{ 1 - \frac{x}{a} \frac{da}{dx} \right\}$$

and

$$A - x \frac{dA}{dx} = x^2 \frac{c}{a} + \frac{1-x}{a} \frac{da}{dx}$$

The first member of equation (φ''') becomes for $x=0$:

$$n - 1 \mp \sqrt{\frac{c}{a_1}}$$

or

$$n - 1 \mp \frac{n - 1}{\sqrt{1 + \varepsilon_1}}$$

and so, whether the sign $-$ or the sign $+$ is chosen, always positive, if as in the case considered, the quantity ε_1 is positive. For $x=1$ the first member of (φ''') becomes equal to:

$$(n - 1) - n \sqrt{\frac{c}{a_2}}$$

or

$$n - 1 - \frac{n - 1}{\sqrt{1 + \varepsilon_2}}$$

This value would be negative when, as will be supposed in a following case, ε_2 is negative $-$ but it is also positive, if as is now the case, ε_2 is positive. If the sign of the value of the first member of (φ''') is different for $x=0$ and $x=1$, then there will be a value of x between 0 and 1 satisfying (φ'''). But in our case the first member of (φ''') has the same sign for $x=0$ and $x=1$. From this it does not follow, of course, that there exists no root for (φ'''), but only that this equation either has no roots or an even number. This equation has no roots when the locus is imaginary $-$ but if the latter exists, as is the case when $1 > \frac{\sqrt{\varepsilon_1} + n\sqrt{\varepsilon_2}}{n-1}$, and when the

locus is a closed figure, then there must be two. If the value of the first member of (φ''') is graphically represented between $x=0$ and $x=1$, the curve representing this value, begins and ends positive.

If this value passes to negative values, it must have an ordinate equal to 0 at least twice, and so also assume a minimum value. Hence if there are two values of x satisfying (φ'''), the equation obtained by differentiating (φ''') with respect to x , must have a root.

Now $\frac{d(\varphi''')}{dx}$ is equal to:

$$-\frac{n}{2} \frac{-x \frac{d^2 A}{dx^2}}{\sqrt{\left\{ A - x \frac{dA}{dx} \right\}}} \mp \frac{1}{2} \frac{(1-x) \frac{d^2 A}{dx^2}}{\sqrt{\left\{ A + (1-x) \frac{dA}{dx} \right\}}}$$

So for the minimum value of (φ''') this equation must be equal to 0.

This expression is equal to 0, if $\frac{d^2 A}{dx^2} = 0$, or if:

$$\frac{nx}{\sqrt{\left(A - x \frac{dA}{dx}\right)}} = \pm \frac{1-x}{\sqrt{\left\{A + (1-x) \frac{dA}{dx}\right\}}}$$

The latter can only be the case, if in the second member the sign $+$ is retained, and $-$ is rejected. This means that in the expression:

$$n = \frac{1 \pm \sqrt{\left\{A + (1-x) \frac{dA}{dx}\right\}}}{1 - \sqrt{\left\{A - x \frac{dA}{dx}\right\}}}$$

only the sign $+$ must hold in the numerator of the second member, or that $\frac{b_2}{v} > 1$. So if the closed curve is restricted to volumes smaller than b_2 .

If we seek the value of x which satisfies:

$$\frac{n^2 x^2}{A - x \frac{dA}{dx}} = \frac{(1-x)}{A + (1-x) \frac{dA}{dx}}$$

then when this value of x is substituted, (φ''') must be negative, because (φ''') has proved to be positive for $x = 0$ and $x = 1$.

For it is not sufficient for the existence of 2 roots of the equation $\varphi''' = 1$ that φ''' has a minimum value, but it is also required that this minimum value is negative.

If we substitute in:

$$n - 1 - n \sqrt{\left\{A - x \frac{dA}{dx}\right\}} - \sqrt{\left\{A + (1-x) \frac{dA}{dx}\right\}}$$

the value of:

$$\sqrt{\left\{A - x \frac{dA}{dx}\right\}} = \frac{nx}{1-x} \sqrt{\left\{A + (1-x) \frac{dA}{dx}\right\}},$$

then:

$$n - 1 - \frac{n^2 x + (1-x)}{1-x} \sqrt{\left\{A + (1-x) \frac{dA}{dx}\right\}}$$

must be negative.

Now we find from the condition on which φ''' has a minimum value:

$$\frac{dA}{dx} = A \frac{(1-x)^2 - n^2 x^2}{x(1-x)\{1-x+n^2 x\}}$$

and

$$A + (1-x) \frac{dA}{dx} = A \frac{(1-x)^2}{(1-x+n^2x)x(1-x)} = \frac{c}{a} \frac{(1-x)^2}{1-x+n^2x}$$

Hence

$$(n-1) - \sqrt{\frac{c}{a} \{1-x+n^2x\}}$$

must be negative.

Now if we write $a = a_1(1-x) + a_2x - cx(1-x)$ and $\frac{a_1}{c} = \frac{1+\varepsilon_1}{(n-1)^2}$

and $\frac{a_2}{c} = n^2 \frac{1+\varepsilon_2}{(n-1)^2}$, then

$$(n-1) - (n-1) \sqrt{\frac{1-x+x^2x}{(1-x)(1+\varepsilon_1) + xn^2(1+\varepsilon_2) - (n-1)^2 x(1-x)}}$$

must be negative. This will be the case if under the radical sign the numerator is larger than the denominator, or if:

$$(1-x)(1+\varepsilon_1) + n^2x(1+\varepsilon_2) - (n-1)^2 x(1-x) < 1-x+n^2x$$

or

$$(1-x)\varepsilon_1 + n^2x\varepsilon_2 - (n-1)^2 x(1-x) < 0$$

or

$$\frac{\varepsilon_1}{(n-1)^2} - x \left\{ 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2} \right\} + x^2 < 0.$$

The extreme values of x of the closed curve are given by the equation:

$$\frac{\varepsilon_1}{(n-1)^2} - x \left\{ 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2} \right\} + x^2 = 0.$$

If the first member of this equation is negative, the values of x satisfying the same value, are nearer together, as was to be expected.

We have reduced the condition that φ''' be negative in its minimum value to:

$$\frac{\varepsilon_1}{(n-1)^2} - x \left\{ 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2} \right\} + x^2 = -\Delta,$$

if Δ is a positive quantity. If this is to be the case for real values of x , then (ε_1 and ε_2 positive),

$$\left\{ 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2} \right\}^2 > \frac{\varepsilon_1}{(n-1)^2}$$

must be, or

$$1 - \frac{\sqrt{\varepsilon_1 + x\sqrt{\varepsilon_2}}}{n-1} > 0.$$

This condition is fulfilled when the points of which ε_1 and ε_2 are

the coordinates, lie in the region for which the locus considered is a closed curve.

So we may sum up what has been demonstrated as follows. We have derived $\frac{d(\psi''')}{dx} = 0$ from $(\psi''') = 0$, and stated the condition on

which ψ''' becomes negative by the substitution of $\frac{d\psi'''}{dx} = 0$. Strictly

speaking we should still have to show that $\frac{d\psi'''}{dx} = 0$ has real roots

— and moreover that the value of these roots is in accordance with the result obtained. Let us, for this purpose, examine what follows concerning the value of x which satisfies the equation obtained

before, which we derived from $\frac{d\psi'''}{dx} = 0$, viz.

$$\frac{dA}{dx} = A \frac{(1-x)^2 - n^2 x^2}{x(1-x)[1-x+n^2 x]}$$

Now $\frac{dA}{dx} = \frac{c[a_1(1-x)^2 - a_2 x^2]}{a^2}$ and $A = \frac{cx(1-x)}{a^2}$ and after reduction we find:

$$\frac{-a_1 n^2 + a_2}{c} = (1-x)^2 - n^2 x^2$$

or

$$\frac{n^2(\varepsilon_2 - \varepsilon_1)}{(n-1)^2} = (1-x)^2 - n^2 x^2$$

For x between 0 and 1 the second member of this equation has a value of n which descends continually and lies between 0 and $-n^2$. So there will be a root if $\frac{n^2(\varepsilon_2 - \varepsilon_1)}{(n-1)^2} < 1$ and $> -n^2$. Or if

$$\varepsilon_1 > \varepsilon_2 - \left(\frac{n-1}{n}\right)^2$$

and

$$\varepsilon_1 < \varepsilon_2 + (n-1)^2$$

If we trace two lines at an angle of 45° with the axes through the points P and Q , then $\varepsilon_1 < \varepsilon_2 + (n-1)^2$ and $\varepsilon_1 > \varepsilon_2 - \frac{(n-1)^2}{x^2}$

implies that $\frac{dA}{dx}$ has one real root between $x = 0$ and $x = 1$ for all

points between these two lines. If we confine ourselves to positive values of ε_1 and ε_2 , this space comprises a very large part of the first parabola, and moreover the space which I shall indicate by OPQ

between the parabola and the axes. If we put $(1-x)^2 = \frac{n^2\varepsilon_2+k}{(n-1)^2}$ and $n^2x^2 = \frac{n^2\varepsilon_1+k}{(n-1)^2}$, these two equations, when k has been properly determined, will hold for the value of x of the root. By application of $(1-x) + x = 1$, we bring the condition for the determination of k in the following form:

$$\frac{n\sqrt{\varepsilon_2 + \frac{k}{n^2}}}{n-1} + \frac{\sqrt{\varepsilon_1 + \frac{k}{n^2}}}{n-1} = 1.$$

If for the binary mixture ε_1 and ε_2 were such that:

$$\frac{n\sqrt{\varepsilon_2}}{n-1} + \frac{\sqrt{\varepsilon_1}}{n-1} = 1$$

the point $(\varepsilon_1, \varepsilon_2)$ lies on the parabola, and the whole locus reduces to a point. But then it appears that for the root of $\frac{d(\varphi''')}{dx} = 0$ the quantity k must be $= 0$, and that the value of x for this root coincides with the point in which the locus has contracted. If ε_1 and ε_2 have such a value that $\frac{n\sqrt{\varepsilon_2}}{n-1} + \frac{\sqrt{\varepsilon_1}}{n-1} < 1$, the point $\varepsilon_1, \varepsilon_2$ lies in the space OPQ , and there is a locus between two values x_1 and x_2 . If we add $\frac{k}{n^2}$ both to ε_1 and to ε_2 , then $\frac{k}{n^2}$ may be chosen in such a way that the condition $\frac{d(\varphi''')}{dx} = 0$ is satisfied, and so also:

$$\frac{n\sqrt{\varepsilon_2 + \frac{k}{n^2}}}{n-1} + \frac{\sqrt{\varepsilon_1 + \frac{k}{n^2}}}{n-1} = 1 .$$

The addition of an equal amount to ε_1 and to ε_2 involves, of course, a shifting of the point $(\varepsilon_1, \varepsilon_2)$ in a direction which makes an angle of 45° with the axes, and that in such a way that the projection of the shifting on each of the axes is equal to $\frac{k}{n^2}$. We suppose k to be positive. So we find the value of k by taking n^2 times the amount which is to be added to the projections of the said point to reach the parabola. If the point $(\varepsilon_1, \varepsilon_2)$ lies in OPQ , k is positive. But for points within the parabola, k is negative. But as for the case that the closed locus exists, the point $(\varepsilon_1, \varepsilon_2)$ must lie inside OPQ , we have only to deal with positive values of k .

So we have $x > \frac{\sqrt{\varepsilon_1}}{n-1}$ and $1-x > \frac{n\sqrt{\varepsilon_2}}{n-1}$, and the equation :

$$\frac{\varepsilon_1}{(n-1)^2 x} + \frac{n^2 \varepsilon_2}{(n-1)^2 (1-x)} = 1$$

holding for the values of x of the points of the locus, we find, after substitution of $x > \frac{\sqrt{\varepsilon_1}}{n-1}$ and $1-x > \frac{n\sqrt{\varepsilon_2}}{n-1}$:

$$\frac{\sqrt{\varepsilon_1}}{n-1} + \frac{n\sqrt{\varepsilon_2}}{n-1} < 1$$

a relation which exists indeed for points of the space OPQ below the parabola.

But now we have to make the following remark about the equation which indicates the value of x for the points where $\frac{dv}{dx} = 0$ for the closed curve. For this equation (φ''') we found the following form :

$$n-1-n\sqrt{\left\{A-x\frac{dA}{dx}\right\}} \mp \sqrt{\left\{A+(1-x)\frac{dA}{dx}\right\}} = 0$$

or

$$(n-1)-nx\sqrt{\frac{c}{a}\left\{1+\frac{1-x}{a}\frac{da}{dx}\right\}} \mp (1-x)\sqrt{\frac{c}{a}\left\{1-\frac{x}{a}\frac{da}{dx}\right\}} = 0.$$

If we seek the values of $\frac{a+(1-x)\frac{da}{dx}}{a}$ and of $\frac{a-x\frac{da}{dx}}{a}$, we find $\frac{a_2-c(1-x)^2}{a}$ and $\frac{a_1-cx^2}{a}$ for this. These quantities must be positive, because they occur under the radical sign. And this gives a restriction for the values of x for which $\frac{dv}{dx}$ can be $= 0$. If $a_2 > c$ the former of the values mentioned is positive for all the values from $x=0$ to $x=1$. The quantity $\frac{a_2}{c}$ is equal to $\frac{n^2(1+\varepsilon_2)}{(n-1)^2}$, and so certainly greater than 1 for positive ε_2 . The quantity $a_1 - cx^2$ is positive, when $x^2 < \frac{a_1}{c}$ and negative for $x^2 > \frac{a_1}{c}$. So if $\frac{a_1}{c} < 1$, values of x lying near 1, cannot exist. This will be the case, as soon as $1 > \frac{a_1}{c}$ or $1 > \frac{1+\varepsilon_1}{(n-1)^2}$, or $n^2 - 2n > \varepsilon_1$. If we put the

greatest value of x at which $\frac{dv}{dx} = 0$ can still occur $= x_g$, then $1 + \varepsilon_1 = x_g^2 (n-1)^2$ $\varepsilon_1 = x_g^2 (n-1)^2 - 1$, which value must be positive for ε_1 .

Now we may proceed to demonstrate that the minimum of (φ''') cannot be given by the second factor of $\frac{d(\varphi''')}{dx} = 0$, viz. by $\frac{d^2 A}{dx^2} = 0$; and at the same time furnish a proof for the theorem that $\frac{dv}{dx} = 0$ can only occur for volumes smaller than b_2 . The quantity $A = \frac{x(1-x)c}{a}$ begins with a value $= 0$ at $x = 0$, and ends also with 0 at $x = 1$. So there is a maximum value and we find it from $\frac{dA}{dx} = \frac{c[a_1(1-x)^2 - a_2x^2]}{a^2}$ at $\frac{x}{1-x} = \sqrt{\frac{a_1}{a_2}}$. For this maximum value of A $\frac{d^2 A}{dx^2} < 0$, and we should be apt to suppose that this will be the case throughout the course from $x = 0$ to $x = 1$. This, however, is not always the case. In some cases a point of inflection appears in the line representing A at certain value of x , and then $\frac{d^2 A}{dx^2}$ is positive for greater value of x . If we calculate $\frac{d^2 A}{dx^2}$, we may reduce it to the following form :

$$\frac{d^2 A}{dx^2} = -\frac{2c}{a^3} \left\{ a_1 a_2 - c[a_1(1-x)^3 + a_2 x^3] \right\}$$

And now it is the question whether $a_1 a_2 - [a_1(1-x)^3 + a_2 x^3]$ can be equal to 0 . For $x = 0$ this quantity is $a_1[a_2 - c]$, and as $\frac{a_2}{c} = \frac{n^2(1+\varepsilon_2)}{(n-1)^2}$, the value of $a_2 - c$ will certainly be positive for positive ε_2 . Hence $\frac{d^2 A}{dx^2}$ is negative for $x = 0$. For $x = 1$ this quantity is $a_2(a_1 - c)$ and as $\frac{a_1}{c} = \frac{1+\varepsilon_1}{(n-1)^2}$ and $\frac{a_1}{c} - 1 = \frac{1+\varepsilon_1}{(n-1)^2} - 1$, we can get a negative value for it if the value of ε_1 is small and that of n large. This case occurs when $\varepsilon_1 < n^2 - 2n$. Then there is a value of x for which $\frac{d^2 A}{dx^2}$ changes the negative sign into the positive one. Now we saw, however, above, that if $\varepsilon_1 < n^2 - 2n$, the value of $(\varphi''') = 0$ is not real over the full extent from $x = 0$ to $x = 1$. And now the question rises which value of x is greater: the value

at which φ''' becomes imaginary or the value of x at which $\frac{d^2 A}{dx^2}$ becomes $= 0$. We can decide this at once by substituting $x_g = \sqrt{\frac{a_1}{c}}$, the limiting value for (φ''') real, in $\frac{d^2 A}{dx^2}$. We find then:

$$\begin{aligned} \frac{d^2 A}{dx^2} &= -2 \frac{c^3}{a^3} \left\{ \frac{a_1 a_2}{c c} - \left[\frac{a_1}{c} (1-x)^3 + \frac{a_2}{c} x^2 \right] \right\} = \\ &= -2 \frac{c^3}{a^3} \left\{ x_g^2 \frac{a_2}{c} - x_g^2 (1-x_g)^2 - x_g \frac{a_1}{c} \right\} \end{aligned}$$

or

$$\frac{d^2 A}{dx^2} = -\frac{2c^3}{a^3} x_g^2 (1-x_g) \left\{ \frac{a_2}{c} - (1-x_g) \right\}$$

As $\frac{a^2}{c} > 1$, and a fortiori $> (1-x_g)$, we find $\frac{d^2 A}{dx^2}$ still negative.

Finally by availing ourselves of the values obtained we shall be able to verify that even if the function (φ'') is not real over the full extent from $x=0$ to $x=1$, and so if our conclusion that this function must possess a minimum value which is negative, can no longer be considered as proved, there is even in this case also a root for $\frac{d(\varphi'')}{dx} = 0$ at a value of x which is smaller than x_g , and which has therefore the former meaning for (φ') .

For the root of $\frac{d(\varphi''')}{dx} = 0$ holds the equation:

$$\frac{a_2 - n^2 a_1}{c} = (1-x)^2 - n^2 x^2 \quad (\text{see page 431})$$

and so if $\frac{a_1}{c} = x_g^2$ is put, the following equation holds:

$$\frac{a_2}{c} - (1-x_g)^2 = (1-x)^2 - (1-x_g)^2 + n^2 (x_g^2 - x^2)$$

or

$$\frac{a_2}{c} - (1-x_g)^2 = (x_g - x) \{ 2 + (n^2 - 1)(x_g + x) \}$$

and as $\frac{a_2}{c} - (1-x_g)^2$ is positive, $(x_g - x)$ must also be positive, or the root of $\frac{d(\varphi''')}{dx} = 0$ lies at smaller value of x than that of the final

point of (φ''') . At the final point $(\varphi''') = 0$. At $x = 0$, (φ''') is positive. So for the intermediate minimum value (φ''') is negative.

The function $\varphi''' = 0$, the relation through which we may know the value of x for the points in which $\frac{dv}{dx} = 0$ for the closed curve, must also be satisfied by the value of x of the point in which the closed curve has contracted to a single point. To show this we have to substitute the values $x = \frac{\sqrt{\varepsilon_1}}{n-1}$ and $(1-x) = \frac{\sqrt{\varepsilon_2}}{n-1}$ in:

$$(n-1) - nx \frac{c}{a} (1-x) \sqrt{\left[\frac{a_2}{c(1-x)^2} - 1 \right]} - (1-x) \frac{xc}{a} \sqrt{\frac{a_2}{cx^2} - 1} = 0$$

where it appears that this equation is satisfied. That we only retain the sign — for the third term is in accordance with our conclusion

that $v < b_2$ for the whole curve. And that $\frac{dv}{dx} = 0$ must also be satisfied in the isolated point, — the point to which the whole curve

has contracted, — follows from the circumstance that for such a point

$\frac{dv}{dx}$ has an arbitrary value. The quantity $\frac{a}{cx(1-x)} = \frac{1}{A}$ is equal to:

$$\frac{a_1(1-2(+\alpha_2x-cx1-2))}{cx(1-x)} = \frac{a_1}{cx} + \frac{a_2}{c(1-x)} - 1 = \frac{1+\varepsilon_1}{(n-1)\sqrt{\varepsilon_1}} + \frac{n(1+\varepsilon_2)}{(n-1)\sqrt{\varepsilon_2}} - 1$$

or

$$\frac{a}{cx(1-x)} = \frac{1}{\sqrt{\varepsilon_1}} + \frac{n}{\sqrt{\varepsilon_2}}$$

$$\text{Further } \sqrt{\frac{a_2}{c(1-x)^2} - 1} = \sqrt{\frac{1}{\varepsilon_2}} \text{ and } \sqrt{\frac{a_1}{cx^2} - 1} = \sqrt{\frac{1}{\varepsilon_1}}$$

Substituting these values we find:

$$(n-1) - \frac{(n-1)}{\frac{1}{\sqrt{\varepsilon_1}} + \frac{n}{\sqrt{\varepsilon_2}}} \left[\frac{n}{\sqrt{\varepsilon_2}} + \frac{1}{\sqrt{\varepsilon_1}} \right] = 0$$

Let us write the equation of the closed curve in the following form:

$$\left(\frac{v}{b}\right)^2 (1-A) - 2\frac{v}{b} + (1+B) = 0,$$

$$\text{representing by } B \frac{\left(\frac{db}{dx}\right)^2 x(1-x)}{b^2} = \frac{(n-1)^2 x(1-x)}{(1-x)^2 + 2nx(1-x) + n^2x^2}.$$

Let us seek the points of this curve for which $\frac{d}{dx} \frac{v}{b} = 0$. Such a point lies for the branch of the small volumes on the right of the point for which $\frac{dv}{dx} = 0$, and on the left for the branch of the larger volumes. By differentiating the equation of the curve in the last mentioned form with respect to x , and keeping $\frac{v}{b}$ constant, we find as a condition:

$$-\left(\frac{v}{b}\right)^2 \frac{dA}{dx} + \frac{dB}{dx} = 0,$$

or

$$\frac{v}{b} = + \frac{\sqrt{\frac{dB}{dx}}}{\sqrt{\frac{dA}{dx}}},$$

from which it appears that $\frac{dA}{dx}$ and $\frac{dB}{dx}$ must have the same sign for such points. Now $\frac{dA}{dx} = \frac{c \{a_1(1-x)^2 - a_2v^2\}}{a^2}$ and for $\frac{dB}{dx}$ we find the value $\frac{(n-1)^2 \{(1-x)^2 - n^2x^2\}}{(1-x+nx)^4}$. So $\frac{1-x}{x} \leq \sqrt{\frac{a_1}{a_2}}$ must go together with $\frac{1-x}{x} \leq \frac{1}{n}$; or $\frac{x}{1-x} \leq \frac{1}{n}$ and $\frac{x}{1-x} \leq \frac{1}{n} \sqrt{\frac{1+\varepsilon_1}{1+\varepsilon_2}}$ must hold at the same time. What it depends on whether $\frac{dB}{dx}$ and $\frac{dA}{dx}$ is positive or negative, is seen when the value obtained for $\frac{v}{b}$ is substituted in the equation of the curve. If we write this as follows:

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

we find:

$$\left(\sqrt{\frac{\frac{dB}{dx}}{\frac{dA}{dx}}} - 1\right) = \pm \sqrt{\frac{A \frac{dB}{dx} - B}{\frac{dA}{dx}}}$$

or

$$\left(\sqrt{\frac{\frac{dB}{dx}}{\frac{dA}{dx}} - 1} \right) = \sqrt{\frac{A^2}{\frac{dA}{dx}} \frac{d\left(\frac{B}{A}\right)}{dx}}$$

And as $\frac{B}{A} = \frac{(b_2 - b_1)^2 a}{c b^2}$ and $\frac{a}{b^2} = 27 p_{kr}$, it appears that $\frac{dA}{dx}$ and so also $\frac{dB}{dx}$ have the same sign as $\frac{dp_{kr}}{dx}$. So if $\frac{a_2}{b_2^2} > \frac{a_1}{b_1^2}$ or $\varepsilon_2 > \varepsilon_1$, then $\frac{dA}{dx}$ and $\frac{dB}{dx}$ is positive, and vice versa. The line which divides the angle between the axes into two equal parts in fig. 36 or joins point O' with point O in fig. 37, gives the division between $\varepsilon_2 \gtrless \varepsilon_1$. For $\frac{dp_{kr}}{dx} > 0$, $p_{kr_2} > p_{kr_1}$ or $\frac{a_2}{b_2^2} > \frac{a_1}{b_1^2}$ and $\varepsilon_2 > \varepsilon_1$. This is the case for all points lying right of this line — and the other way about. For the points of this line themselves $\varepsilon_2 = \varepsilon_1$ or $\frac{dp_{kr}}{dx} = 0$. But then also $\frac{dA}{dx}$ and $\frac{dB}{dx} = 0$ and so $\frac{x}{1-x} = \frac{1}{n}$, or what is the same thing

$$\frac{x}{1-x} = \sqrt{\frac{a_1}{a_2}} = \frac{1}{n} \sqrt{\frac{1+\varepsilon_1}{1+\varepsilon_2}}$$

But, as we already observed above, this requires that the value l^2 be greater than 1 in the formula $l^2 n^2 (1 + \varepsilon_1)^2 = \left[n + \frac{1+n^2}{2} \varepsilon_1 \right]$ or $ln(1 + \varepsilon_1) = n \frac{1+n^2}{2} \varepsilon_1$. Then we have:

$$l = \frac{1 + \frac{1+n^2}{2n} \varepsilon_1}{1 + \varepsilon_1}$$

or

$$l - 1 = \frac{(n-1)^2}{2n(1 + \varepsilon_1)} \varepsilon_1.$$

Now for the area OPQ , under the parabola we have

$$(1+n) \sqrt{\varepsilon_1} \leq n - 1$$

and so ε_1 can become equal to $\left(\frac{n-1}{n+1}\right)^2$ as highest value, and hence

$(l-1)_{max} = \frac{(n-1)^4}{4n(n^2+1)}$. For not very high value of n , $l-1$ is only

small. So $l-1$ is equal to $\frac{1}{40}$ e.g. for $n=2$. For $n=3$, $l-1 = \frac{2}{15}$

But this is no longer the case for high value of n . We need not fear in any case, however, that l will become so great that $a_1 + a_2 - 2a_{1,2}$ would become < 0 . That c be > 0 , the following equation must hold:

$$2a_{1,2} < a_1 + a_2$$

or

$$2l \sqrt{a_1 a_2} < a_1 + a_2$$

or

$$2l < \sqrt{\frac{a_1}{a_2}} + \sqrt{\frac{a_2}{a_1}}$$

or

$$2l < \frac{1}{n} \sqrt{\frac{1+\varepsilon_1}{1+\varepsilon_2}} + n \sqrt{\frac{1+\varepsilon_2}{1+\varepsilon_1}}$$

or in our case

$$2l < n + \frac{1}{n}$$

or

$$(l-1) < \frac{(n-1)^2}{2n}$$

Now

$$(l-1) = \frac{(n-1)^2}{2n} \frac{\varepsilon_1}{1+\varepsilon_1}$$

Hence $(l-1)_{max}$ remains also below the value, which would make $a_1 + a_2 - 2a_{1,2}$ equal to 0.

But now before proceeding to the comparison of the results obtained here with those of the experiment, I shall first have to discuss the question whether the disappearance of the intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ really involves the disappearance of the complication in the spinodal line, — and so whether the temperature at which the two curves mentioned touch, is at the same time the temperature at which the pair of *heterogeneous* plaitpoints occurring in the spinodal line, coincide. When the points of intersection of the two curves approach each other, the two *heterogeneous* plaitpoints will, no doubt, also come nearer to each other. But it need not follow from this that when the points of intersection coincide, also the pair of plaitpoints coincide. And à priori it is unlikely that this should be the case. The existence or non-existence of points of intersection depends only on properties of the two curves, without a third curve

$\frac{d^2\psi}{dx dv} = 0$ being able to exert any influence on this. But the course of the spinodal line is the result of properties of $\frac{d^2\psi}{dx^2} = 0$ as well as of $\frac{d^2\psi}{dv^2} = 0$ and of $\frac{d^2\psi}{dx dv} = 0$; from this it may already be expected that when the curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ touch, the two *heterogeneous* plaitpoints will occur on the spinodal line, and will lie at some distance from each other. If this is so, this means that the limits for the existence and disappearance of the heterogeneous plaitpoints are wider apart than the temperatures at which the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ begin to intersect and stop doing so; and à fortiori this is the case for the limits of the temperature of their appearance and disappearance on the binodal line, and so also for the limits of the temperature for the existence of three-phase-pressure. And that this is true may be seen when we more closely examine the peculiarities which occur in the course of the spinodal line in the case that the two curves still intersect. Let us imagine the circumstances as in fig. 12, Vol. IX, p. 846, Contribution III, viz. the line $\frac{dp}{dx_v} = 0$ at smaller volume than the line $\frac{dp}{dv} = 0$; but preferably at somewhat lower temperature, so that at $x = 0$ the two branches of $\frac{dp}{dv} = 0$ are still separated.

Then the isobars enter the figure at $x = 1$, have $\frac{dv}{dx_p}$ negative, and in the neighbourhood of $\frac{dp}{dv} = 0$ they incline towards this curve which they intersect in a direction parallel to the axis of v . So the quantity $\frac{d^2v}{dx^2_p}$ is positive. For the q -lines the quantity $\frac{d^2v}{dx^2_q}$ is negative in the neighbourhood of $\frac{dp}{dv} = 0$. So in a point of contact of the p - and q -lines, a point of the spinodal line (see Vol. IX p. 747 Contr. II), $\left(\frac{dv}{dx}\right)_{spin}$ is positive according to the formula:

$$\left(\frac{dv}{dx}\right)_{spin} = \left(\frac{dv}{dx}\right)_{p=q} \frac{\left(\frac{d^2v}{dx^2}\right)_q}{\left(\frac{d^2v}{dx^2}\right)_p}$$

And according to the formula Vol. IX p. 749, Contribution II):

$$\left(\frac{dp}{dx}\right)_{spm} = \left(\frac{dp}{dx}\right)_v \left\{ 1 - \frac{\left(\frac{d^2v}{dx^2}\right)_q}{\left(\frac{d^2v}{dx^2}\right)_p} \right\}$$

$\left(\frac{dp}{dx}\right)_{spm}$ has the same sign as $\left(\frac{dp}{dx}\right)_v$, and is therefore negative. In the point of contact the two lines p and q do not intersect. The p -line lies in the point of contact on the same side of the q -line -- e. g. on the lower side. But in fig. 12 contact of a p - and a q -line has again been drawn on the left side of $\frac{d^2\psi}{dx^2} = 0$. But there the p -line remains above the q -line all through. -- So there must be a point of contact somewhere between, where there is a transition between these two cases, and where the contact is at the same time intersection. Then not only $\frac{dv}{dx_p} = \frac{dv}{dx_q}$, but $\frac{d^2v}{dx^2_p} = \frac{d^2v}{dx^2_q}$ and so also $\frac{dp}{dx} = 0$. Then we are in a plaitpoint. If taking due account of the course of the p - and q -lines, we seek this plaitpoint it appears that this point does not lie on that particular q -line that passes through the highest point of the curve $\frac{d^2\psi}{dx^2} = 0$, and has there a direction parallel to the x -axis, and also possesses there a point of inflection. But it lies on a q -line lying left of the former, where p has a greater value; while this plaitpoint must lie below the point of inflection of the q -line, because $\frac{d^2v}{dx^2_p}$ is always positive.

Of course, but this is not necessary for our argument, if for points of the spinodal line with very small x , the contact of the q - and p -lines is to take place again in such a way that the p -line remains again throughout on the same side of the q -line, which we may also call the lower side, there must exist another plaitpoint also on the left hand of $\frac{d^2\psi}{dx^2} = 0$. So in this second plaitpoint the p -line, coming from the right, must first run above the q -line, which it will touch, and will be below it from the point of contact. What is indeed essential for our argument, is the circumstance that the first-mentioned plaitpoint, the upper of the pair of heterogeneous plaitpoints, which I called the realizable one in a previous Contribution, though it only fully deserves this name when it also lies above the binodal curve, lies on an isobar of higher value of the pressure than the

value of p found in the point in which $\frac{d^2\psi}{dv^2} = 0$ has the smallest volume. And if we now consider the case that the whole closed curve discussed above, has contracted to a single point, and the intersection of the two curves $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^3\psi}{dv^3}$ has disappeared, and the q -line runs parallel to the x -axis in that single point and possesses there a point of inflection, the realizable plaitpoint still exists, and so also the other, the hidden one. A fortiori this is the case when the closed curve still exists, and the intersection of the two curves, $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^3\psi}{dv^3} = 0$ has only disappeared because they touch. For then the q -line, which passes through the point of contact, will still possess the points with maximum and minimum volume, and it will lie below the q -line where they have coincided.

So we are justified in the following graphical representation. Let us take an x -axis and a p -axis. Let us construct a figure indicating first the pressure along the liquid branch of the line $\frac{d^2\psi}{dv^2} = 0$, and secondly the pressure along the liquid branch of the spinodal line. Not to interrupt our train of reasoning too much, we shall pass over the other branches in silence, and moreover confine ourselves to the case in which $T_{k_2} > T_{k_1}$. Then the first-mentioned line is a continually descending one. If the temperatures are low — according to the approximate equation of state below $^{27}/_{32} T_k$ — all the points of this line lie below the x -axis. But as we only wish to consider the relative position of the two curves which are to be represented we disregard the absolute height at which we think them drawn. The second line begins and terminates as high as the first, and always remains above it. So in the main it is also a fast descending line. Now if there are on the first line two points, indicating the points of intersection of the line $\frac{dp}{dv} = 0$ with $\frac{d^2\psi}{dv^2} = 0$, the second line will not continually descend, but possess a minimum and a maximum value for p . The minimum value at a value of x which is smaller than the value of x of the first point of intersection, and the maximum value at a value of x , which is greater than that of the second point of intersection. This minimum and this maximum value are those of the pair of *heterogeneous* plaitpoints. If the two points of intersection have coincided on the first-mentioned line, minimum and maximum pressure still occurs on the second. And

only at a temperature, at which either there is not yet question of contact of the two curves $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dv^2}$, or at which this contact is long over, the complication in the course of the p -line will have disappeared for the spinodal line. At the moment of the disappearance this p -line possesses a horizontal tangent and a point of inflection in the point in which maximum and minimum pressure coincide. If further in such a figure we drew a third line indicating the pressure along the binodal curve, this third line would have a complicated shape — but for this I refer to some Communications occurring in These Proceedings 1905.

But from all this we further conclude that is not necessary that the two curves $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ intersect for the occurrence of the pair of heterogeneous plaitpoints on the spinodal line. If they only draw near enough to each other, the spinodal line can already possess the described complication, and there can even be three-phase-pressure.

It follows from this that for mixtures the properties of whose components are represented besides by n , by positive ε_1 and ε_2 , the presence of the heterogeneous plaitpoints is not restricted to the space OPQ below the parabola for ε_1 and ε_2 ; but that this space must be extended with a part of the parabola itself — a part lying in the neighbourhood of the top. The theoretically exact shape of this part can only be determined by investigation of the spinodal line itself. But in view of the difficulties attending this investigation, I shall content myself here with an indication of the way in which I have tried to form an idea for myself of the accuracy of my expectations that this part would again be approximately bounded by a parabola, which compared to the preceding one, would have shifted in the direction of the axis, though what follows must not be looked upon as much more than a certain kind of empirical calculation. When the curve $\frac{d^2\psi}{dv^2} = 0$ lies entirely within $\frac{d^2\psi}{dv^2} = 0$, but in the neighbourhood of the latter curve, two other curves, viz. $\frac{d^2\psi}{dv^2} = 0$ at lower temperature, and $\frac{d^2\psi}{dv^2} = 0$ at another still lower temperature will show intersection and contact in the space outside $\frac{d^2\psi}{dv^2} = 0$, where the spinodal curve lies, and where the pair of heterogeneous plaitpoints are found, at a certain distance apart or coinciding.

If in $\frac{d^2\psi}{dv^2} = 0$ we take the lower temperature $T' = \frac{T}{k}$, and in $\frac{d^2\psi}{da^2} = 0$ the value of the lower temperature $T'' = \frac{T}{k'}$, we obtain by elimination of T , the equation, which with a slight modification agrees with (2) of Contribution X:

$$v^2 \left\{ 1 - v(1-v) \frac{k'}{k} \frac{\frac{d^2a}{da^2}}{2a} \right\} - 2bv + \left\{ b^2 + v(1-v) \left(\frac{db}{da} \right)^2 \right\} = 0.$$

If we now treat this equation in the same way as (a) was treated in Contribution X, we get, for the case that the closed curve contracts to one point, the condition:

$$n - 1 = \sqrt{\left(\varepsilon_1 - \frac{k' - k}{k} \right)} + n \sqrt{\left(\varepsilon_2 - \frac{k' - k}{k} \right)}.$$

So the same parabola as before, only shifted in the direction of the two axes by an amount equal to $\frac{k' - k}{k}$.

The value of T at which the imitated plaitpoints coincide in this calculation, is now k or k' times higher.

(To be continued).

E R R A T U M.

In the proof that the closed curve, the locus of the points of intersection of $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{da^2} = 0$, always lies at $v < b_2$, a possible case has been overlooked. The value $v < b_2$ may occur if:

$$n - 1 > \sqrt{1 + \varepsilon_1} + n \sqrt{\varepsilon_2},$$

as will be shown in the *Continuation*.

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