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x_0 , x_m diameters of the rings in *m.m.*
x_0 mean of 2 diameters on plates taken before and after x_m.
First ring:

$x_0 = 3.662$	$x_0^2 = 13.410$	0.160	
$x_m = 3.640$	$x_m^2 = 13\ 250$		
Second ring:			0.171
$x_0 = 2.608$	$x_0^2 = 6.802$	0.182	
$x_m = 2.573$	$x_m^2 = 6\ 620$		

$$\Delta \lambda_0 = \frac{0.171 \lambda_0}{8 R^2} = 0.0086 \text{ Å. E.}$$

In the case of the triplet of the mercury line 5770 no displacement of the central line could be found. In a field of 28250 the following values of the diameters were obtained with the 5 m.m. étalon:

First ring	Second ring	
2.199	3.409	field off.
2.193	3.408	field on.
2.199	3.394	field off.

Hence the central line of 5770 remains within the limits of experimental error exactly in the position of the unmodified one.

Physics. — "*Contribution to the theory of binary mixtures,*" XII. (Continued). By Prof. J. D. VAN DER WAALS.

In the discussion in the preceding contribution on the question whether there is any possibility that values of $v > b_2$ might occur in the case that the locus of the points of intersection of the curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ is a closed curve, we have also discussed (p. 433) the case that (φ''') or:

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

would be imaginary over the full width from $x = 0$ to $x = 1$. We have reduced this equation there to the following form:

$$n - 1 - nx \sqrt{\frac{c}{a}\frac{a_2 - c(1-x)^2}{a}} \mp (1-x)\sqrt{\frac{c}{a}\frac{a_1 - cx^2}{a}} = 0$$

and shown that if $n > 2$, the value of $a_1 - cx^2$ may become negative for the high values of x. The limiting value of x is then equal to $\sqrt{\frac{a_1}{c}}$, so that we have $x_g = \sqrt{\frac{a_1}{c}}$. We then observed (p. 435) that if such a limiting value for x exists, our conclusion that $\varphi''' = 0$ must possess a minimum value which is negative, can no longer be considered as proved; but we omitted the observation that the thesis that v would have to be $< b_2$, may not be considered as proved any longer either. If viz. the substitution of $x = x_g$ should make the first member of (φ''') negative, whereas, as we saw before, the substitution of $x = 0$ makes the first member of (φ''') positive, then a value of x must exist which makes $(\varphi''') = 0$ both on the branch of (φ''') with the negative sign for the third term as on that with the positive sign. Then it is therefore unnecessary, that (φ''') possesses a minimum value, and there is no reason for the positive sign for the third term, and so no necessity for v being smaller than b_2.

Let us seek the condition for:

$$n - 1 - nx_g \frac{\sqrt{\{a_2 - c(1-x_g)^2\}}}{a} < 0$$

or

$$\frac{n-1}{n} < \frac{x_g \sqrt{\frac{a_2}{c} - (1-x_g)^2}}{\frac{a}{c}}$$

Let us write;

$$\frac{a}{c} = \frac{a_1}{c}(1-x_g) + \frac{a_2 x_g}{c} - x_g(1-x_g)$$

or

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

or

$$\frac{a}{c} = x_g \left\{\frac{a_2}{c} - (1-x_g)^2\right\}.$$

The condition put above, becomes then:

$$\frac{n-1}{n} < \frac{1}{\sqrt{\left\{\frac{a_2}{c} - (1-x_g)^2\right\}}}$$

or

$$\frac{a_2}{c} - (1-x_g)^2 < \frac{n^2}{(n-1)^2}$$

or

$$\frac{n^2(1+\varepsilon_2)}{(n-1)^2}-(1-x_g)^2<\frac{n^2}{(n-1)^2}$$

or

$$\frac{n^2\varepsilon_2}{(n-1)^2}-(1-x_g)^2<0$$

or

$$\frac{n\sqrt{\varepsilon_2}}{n-1}<1-x_g.$$

And taking into account that $x_g=\sqrt{\frac{a_1}{c}}=\frac{\sqrt{1+\varepsilon_1}}{n-1}$, we obtain as condition:

$$(n-1)>\sqrt{1+\varepsilon_1}+n\sqrt{\varepsilon_2}.$$

I have given it in this form in the "Erratum" accompanying the preceding Contribution.

Before discussing the signification of this condition I will remark that we might, indeed, have obtained this result in a less intricate way.

Let us directly put the value $v=b_2$ in the equation for the closed curve, and let us examine what value of x then satisfies the equation. If $v=b_2$, then $v-b=(b_2-b_1)(1-x)$, and $v^2=b_2^2$. Equation (α) of Contribution X p. 318 becomes then:

$$\frac{(n-1)^2}{n^2}(1-x)=\frac{c\,x\,(1-x)}{a}$$

or

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

or

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

then we find as condition for the calculation of x for which $v=b_2$:

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

or

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

As $1+\varepsilon_1$ must certainly be positive, because a negative value of a_1 is inconceivable, we see that if the above equation has real roots, it must have two for positive values of x in all possible cases, also if ε_1 and ε_2 should be negative. The condition for the roots being real is:

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

or

$$1-\frac{\sqrt{(1+\varepsilon_1)}}{n-1}>\frac{n\sqrt{\varepsilon_2}}{n-1}.$$

So the same condition as had been found above.

If we represent the condition for the possibility of $v>b_2$ again graphically, it is given by a parabola, and that the same as occurs in fig. 36 p. 321, but shifted downward in the direction of the ε_1-axis by an amount $=1$. We need not draw it, but we shall think the points of contact with the ε_1-axis and with a line $\varepsilon_1=-1$ indicated by the letters Q'' and P''. To satisfy the circumstance $v>b_2$, the point $(\varepsilon_1, \varepsilon_2)$ must lie inside the space which I shall call $O''P''Q''$. But for the possibility of the closed figure the point $(\varepsilon_1, \varepsilon_2)$ must lie inside the space OPQ — in both cases below the corresponding parabola. This can only occur when the two areas mentioned cover each other or as least overlap. This requires $(n-1)^2>1$ or $n>2$. So the points $(\varepsilon_1, \varepsilon_2)$ giving a closed curve, for which the value $v>b_2$ occurs between two values of x, are confined to a smaller space, again bounded by the axes and a parabola. In this case the parabola touches the ε_1-axis at a distance $n(n-2)$ from the origin, but intersects the ε_2-axis at a distance $=\frac{n(n-2)}{n^2}=\frac{n-2}{n}$ from the origin. The condition that the two values of x for which $v=b_2$, coincide, and that the closed curve touch a line $v=b_2$ is this: that the point $(\varepsilon_1, \varepsilon_2)$ shall lie on this parabola. Then $x=\sqrt{\frac{1+\varepsilon_1}{(n-1)^2}}$ and $1-x=\frac{n\sqrt{\varepsilon_2}}{n-1}$. If we compare this value of x with that which we have called x_g above, x_g appears to be besides highest value of x for which $\frac{dv}{dx}$ is equal to 0 for the points of the closed curve, also the value of x for the point in which the closed curve touches the line $v=b_2$. If volumes occur which are larger than b_2, then the greatest volume lies at a value of $x<x_g$.

Let us now more closely examine the space which OPQ and $O''P''Q''$ have in common, and inside which the points $(\varepsilon_1, \varepsilon_2)$ must lie for the condition $v>b_2$ to be satisfied. For n very large this space will be very large in the direction of the ε_1-axis, but in the direction of the ε_2-axis it remains limited to an amount $1-\frac{2}{n}$ and so below unity. Also by simple construction we can now indicate a rule for the place of the points $(\varepsilon_1, \varepsilon_2)$ which satisfy the requirement that the portion cut off by the closed curve from the line $v = b_2$, have a given value.

From equation (β) of p. 479 follows:

$$2x = 1 + \frac{1+\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2} \pm \sqrt{\left\{\left[1 + \frac{1+\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2}\right]^2 - 4\frac{1+\varepsilon_1}{(n-1)^2}\right\}}$$

If we represent the highest value of x by x_2, and the smallest by x_1, then:

$$(x_2 - x_1)^2 = \left[1 + \frac{1+\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2}\right]^2 - 4\frac{1+\varepsilon_1}{(n-1)^2}$$

or

$$2\sqrt{\left\{\frac{1+\varepsilon_1}{(n-1)^2} + \frac{(x_2-x_1)^2}{4}\right\}} = 1 + \frac{1+\varepsilon_1}{(n-1)^2} + \frac{(x_2-x_1)^2}{4} - n^2\left\{\frac{\varepsilon_2}{(n-1)^2} + \frac{(x_2-x_1)^2}{4n^2}\right\}$$

or

$$1 - \sqrt{\left[\frac{1+\varepsilon_1}{(n-1)^2} + \frac{(x_2-x_1)^2}{4}\right]} = n\sqrt{\left[\frac{\varepsilon_2}{(n-1)^2} + \frac{(x_2-x_1)^2}{4n^2}\right]}$$

So the points for which $x_2 - x_1$ has an equal value, lie again on a parabola, and one of the same shape as that of fig. 36; but now it has undergone two shiftings.

The first shifting is that in which all the points of the parabola have descended by an amount $= 1$ in the direction of the ε_1-axis which makes it the upper limit of the space now under discussion. But the second shifting is one which takes place in the direction of the diameter or the axis of the parabola. The amount of the second shifting must be such that it can be considered as the resultant of a displacement in the direction of the negative ε_1 by an amount equal to $\frac{(x_2-x_1)^2}{4}(n-1)^2$ and a displacement in the direction of the negative ε_2-axis by an amount equal to $\frac{(x_2-x_1)^2}{4}\frac{(n-1)^2}{n^2}$. According as $x_2 - x_1$ is greater, this second shifting is more considerable — but as soon as the shifting would proceed so far that the parabola would have no more points inside the original space OPQ we have exceeded the possible value of $x_2 - x_1$. The extreme limits of $x_2 - x_1$ are then on one side 0, and on the other side $1 - \frac{1}{n-1} = \frac{n-2}{n-1}$. This greatest value of $x_2 - x_1$, which is equal to 0 for $n = 2$ itself approaches 1 with increasing value of n. We may also express the above as follows. When we have a point $(\varepsilon_1, \varepsilon_2)$ in the space which OPQ and $O''P''Q''$ have in common, the closed curve will possess volumes which are greater than b_2 — and by shifting this point in the direction of the axis of the parabola till it meets the first-mentioned shifted parabola, we find the value $\frac{(x_2-x_1)^2}{4}(n-1)^2$, in the projection of this displacement on the ε_1-axis, or the value of $\frac{(x_2-x_1)^2}{4}\frac{(n-1)^2}{n^2}$ in the projection of this displacement on the ε_2-axis. So the length of the line drawn through the given point in the direction of the axis of the parabola till it meets the second parabola teaches us the value of $(x_2-x_1)^2$; to which we may add that the same line prolonged to the other side so below the given point, shows us also at what value of x the middle of x_1 and x_2 lies. If the continuation of this line passes through the point $\varepsilon_2 = 0$ and $\varepsilon_1 = -1$, the middle of x_1 and x_2 lies exactly at $x = \frac{1}{2}$. If this line intersects the ε_1-axis below $\varepsilon_1 = -1$, then $\frac{x_1+x_2}{2} < \frac{1}{2}$ and the other way about. We have viz. from (β):

$$x_1 + x_2 = 1 + \frac{1+\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2},$$

or putting $\frac{x_1+x_2}{2} = x_m$:

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

For given value of x_m this represents a straight line, the direction of which is given by $\frac{\varepsilon_1}{\varepsilon_2} = n^2$. This straight line intersects the ε_1-axis in a point $\varepsilon_1 + 1 = -(n-1)^2(1-2x_m)$; from this formula the given rule appears.

Such rules may also be given for the dimension and the place of the closed curve itself — and for the accurate knowledge of the properties of this curve the knowledge of such rules is not devoid of importance. Thus the equation (β') of p. 319 Contribution X leads to:

$$(x_2-x_1)^2 = \left\{1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2}\right\}^2 - \frac{4\varepsilon_1}{(n-1)^2}$$

when the values of x between which the curve exists, are represented by x_1 and x_2. If we derive from this:

$$1 - \sqrt{\left\{\frac{\varepsilon_1}{(n-1)^2} + \frac{(x_2-x_1)^2}{4}\right\}} = n\sqrt{\left\{\frac{\varepsilon_2}{(n-1)^2} + \frac{(x_2-x_1)^2}{4n^2}\right\}}$$

it appears that the locus of the points ε_1 and ε_2 for which the closed curve has the same width, is again the same parabola OPQ, but shifted in opposite direction of the axis by an amount of such a value that the projection on the ε_1-axis is equal to $(n-1)^2 \frac{(x_2-x_1)^2}{4}$. For the points of OPQ itself the width is, therefore, equal to 0, and for the origin, in which ε_1 and ε_2 is equal to 0, $x_2-x_1=1$, and the curve occupies the whole width. The decrease of the values of ε_1 and ε_2 obtained by shifting in the opposite direction of the axis of the parabola, promotes therefore the intersection of $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$, and so furthers the non-miscibility. In the same way we find, representing the value of $\frac{x_1+x_2}{2}$ by x_m:

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

So if we trace a line parallel to the axis of the parabola through the origin, this line is the boundary for the points for which $x_m \gtrless \frac{1}{2}$. For the points for which $\varepsilon_1 > n^2\varepsilon_2$, $x_m > \frac{1}{2}$, and the other way about.

And finally this property. We may also write the equation (β') of p. 319 Contribution X indicating the limiting value of x which corresponds to given value of ε_1 and ε_2 as follows:

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

Let $x = x_1$ for one of these limiting values, then this equation becomes:

$$\frac{\varepsilon_1}{(n-1)^2}\frac{1}{x_1} + \frac{n^2\varepsilon_2}{(n-1)^2}\frac{1}{1-x_1} = 1$$

And for constant value of x_1, this last formula represents a straight line for the points $(\varepsilon_1, \varepsilon_2)$. On this straight line also the point must lie for which not only the one limiting value of $x = x_1$, but also the second, and for which the two values of x therefore coincide. In this case $x_1 = \frac{\sqrt{\varepsilon_1}}{n-1}$ and $1 - x_1 = \frac{n\sqrt{\varepsilon_2}}{n-1}$. Hence we get back again the limiting relation between ε_1 and ε_2 or in other words the equation of the parabola by this substitution in the equation of the straight line. So this straight line is a tangent to the parabola, and one touching in the point in which also the second limiting value of x, or x_2 coincides with x_1. From this follows then this rule. If we draw a tangent to the parabola in the area OPQ, then all the points $(\varepsilon_1, \varepsilon_2)$ for which one of the limiting values is equal to the value for x of the point of contact, lie on this tangent. If we draw a second tangent to the parabola, the point of intersection with the first tangent has the property that the values of x of the two points of contact belong to it for x_1 and x_2. If we have drawn one tangent, tangents may be drawn from all the points of this line lying on the lefthand side of the point of contact, so from all the points for which ε_2 is smaller, and ε_1 larger than that of the point of contact, to the points for which ε_1 is larger, and so $x_2 > x_1$, and the other way about. If we wish to indicate in what part of the space OPQ below the parabola the points lie for which the values of ε_1 and ε_2 are such that the whole closed curve remains restricted either to values of $x > \frac{1}{2}$ or to values of $x < \frac{1}{2}$, we must begin with finding the point on the parabola for which $x_1 = x_2 = \frac{1}{2}$. This is the point for which $\varepsilon_1 = n^2 \varepsilon_2$, and which therefore lies on the line which is drawn from the origin in the direction of the axis of the parabola. In this point we must trace the tangent to the parabola. From the ε_1-axis this tangent cuts off a portion $= \frac{(n-1)^2}{2}$ and from the ε_2-axis a portion $= \frac{(n-1)^2}{2n^2}$. So it is a line parallel to the straight line PQ of fig. 36, and it cuts off from the axes parts equal to $\frac{OP}{2}$ and $\frac{OQ}{2}$. This tangent divides the space OPQ below the parabola into three parts, viz. the part below this tangent, and the two other parts above this tangent and further bounded by the parabola and one of the axes. The righthand one of these two parts contains the points, for which the closed curve remains confined to values of $x < \frac{1}{2}$. For the lefthand part the reverse applies.

So according to this result either of these cases would be possible either that the closed curve remains restricted to values of $x > \frac{1}{2}$, or to values of $x < \frac{1}{2}$. But if it is asked whether it is probable that both cases occur, this probability depends on the value which l^2 must assume in these two cases. The point in which these spaces touch, is the point where $\varepsilon_1 = n^2 \varepsilon_2 = \frac{(n-1)^2}{4}$. For this point to be possible the following equation must hold:

$$(2n + \varepsilon_1 + n^2 \varepsilon_2)^2 = 4 l^2 (1 + \varepsilon_1) n^2 (1 + \varepsilon_2)$$

We find from this by substitution of the values ε_1 and ε_2:

$$l^2 = \frac{(n+1)^4}{(n+1)^4 + 4(n-1)^4}.$$

So in any case a value of $l^2 < 1$. It becomes smaller as n increases, and the limiting value for $n = \infty$ amounts to $\frac{1}{5}$. Such a small value, however, l^2 will most likely never assume. And if we now take into consideration that for the points of the lefthand part, for the points of which $x > \frac{1}{2}$, the value of l^2 will have to be still smaller, we arrive at the conclusion that if n is large, the case that the closed curve remains restricted to values of $x > \frac{1}{2}$ will not have much chance of occurring. For the point in which the two spaces touch l^2 is equal to $\frac{81}{85}$ for $n = 2$, and this value is equal to $\frac{4}{5}$ for $n = 3$, and we may consider these values of l^2 as probably possible. So that we arrive at the conclusion that for not great values of n, e.g. $n = 3$, the closed curve, if it exists, can occur at $x > \frac{1}{2}$, but that for higher values of n, and also if l^2 should be > 1, the other case, $x < \frac{1}{2}$, is possible.

Let us now proceed to derive some results on the miscibility or non-miscibility in the liquid state from what has been observed on the intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$, for the case that the locus of the points of intersection is a closed curve, and to compare these results with the observed facts. All the properties discussed of the closed curve are perhaps no longer necessary if we could have anticipated this result. They have, however, been necessary for me to come to this conclusion. And if we do not content ourselves with more or less vague indications, but want to give clearly defined statements, the knowledge of most of the properties discussed is necessary.

I already treated one of the meanings of the closed curve, p. 331 Contribution X. In this case contact of $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$ occurs for the first time at low temperature T_2; at rising temperature there is intersection of these two curves. But with further rise of T the two points of intersection draw nearer together, and at $T=T_1$ there is again contact. For the case mentioned $\frac{d^2\psi}{dx^2}=0$ had again to lie in the region where $\frac{d^2\psi}{dv^2}=0$ is negative above $T=T_1$. But a second case is possible.

With constantly rising temperature the intersection of the two curves may always proceed in the same sense, and then there can also be contact at $T=T_1$. Then the curve $\frac{d^2\psi}{dx^2}=0$ must disappear in the region where $\frac{d^2\psi}{dv^2}$ is positive. In Contribution III I gave the equation which is to decide whether $\frac{d^2\psi}{dx^2}=0$ is to disappear in the one region or in the other, viz.:

$$\frac{cx_g(1-x_g)}{a} \gtrless \frac{4y_g^2}{1+y_g}.$$

If the sign $>$ holds, $\frac{d^2\psi}{dx^2}=0$ disappears in the region where $\frac{d^2\psi}{dv^2}$ is positive, and the other way about. And now, to answer the question whether the first mentioned case takes place or the second, we must examine this equation, bearing in mind that ε_1 and ε_2 is positive, and that the points $(\varepsilon_1, \varepsilon_2)$ lie below the parabola OPQ.

The values of x_g and y_g are dependent on n, and quite determined by this quantity; and according to the list of calculated values occurring in the beginning of Contribution III, x_g can only vary between $1/3$ and $1/2$, and y_g between $1/2$ and 0. So the second member of the inequality to be investigated is entirely determined by the ratio of the size of the molecules, but the first member depends moreover on ε_1 and ε_2.

Let us write this first member, omitting the index to x_g:

$$\frac{cx(1-x)}{a}=\frac{cx(1-x)}{a_1(1-x)+a_2x-cx(1-x)}=$$

$$\frac{1}{\frac{a_1}{c}\frac{1}{x}+\frac{a_2}{c}\frac{1}{1-x}-1}=\frac{1}{\frac{1+\varepsilon_1}{(n-1)^2}\frac{1}{x}+\frac{n^2(1+\varepsilon_2)}{(n\;\;1)^2(1-x)}-1}$$

or

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

Now there is a series of values of ε_1 and ε_2 (see p. 483) for which the value of $\frac{\varepsilon_1}{(n-1)^2}\frac{1}{x}+\frac{n^2\varepsilon_2}{(n-1)^2}\frac{1}{1-x}-1$ is equal to 0. All these values are given by a line which touches the parabola in a point for which $\frac{\sqrt{\varepsilon_1}}{n-1}=x$, so a point which, as the parabola itself, is entirely determined by the value of n, and lies on the line which passes through the origin in a direction $\frac{\varepsilon_1}{\varepsilon_2}=n^2\left(\frac{x}{1-x}\right)^2$. This direction approaches to $\frac{n^2}{4}$ for very great values of n, and to n^2 itself for values of x which are but little greater than $\frac{1}{2}$. All the values of ε_1 and ε_2 occurring below the parabola are reached when lines are traced parallel to the said tangent. Thus:

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

represents all the points below this tangent, when α is given the negative sign; and then the second member can descend to -1, in which case the origin itself might occur. All the points above the said tangent are reached, when α is given the positive sign, and then made to ascend till $1+\alpha=\frac{1}{x}$, in which case the point Q is reached. For α such that $1+\alpha=\frac{1}{1-x}$, the point P is reached.

So we have for points below the tangent:

$$\frac{cx\,(1-x)}{a}=\frac{1}{\frac{1}{(n-1)^2}\frac{1}{x}+\frac{n^2}{(n-1)^2}\frac{1}{1-x}-\alpha},$$

in which α lies between 0 and 1, and is $=0$ on the tangent itself.

For points above the tangent we have:

$$\frac{cx(1-x)}{a} = \frac{1}{\frac{1}{(n-1)^2}\frac{1}{x} + \frac{n^2}{(n-1)^2}\frac{1}{1-x} + a},$$

in which a lies between 0 and $\frac{1}{x} - 1$; whereas to reach the points lying above the tangent on the side of P we need not go further than $a = \frac{1}{1-x} - 1$. Of course in the same way as illustrated in an example above we have again to consider whether all these points points probably occur by investigating the value of l^2.

The form in which $\frac{cx(1-x)}{a}$ has been given, now consists of two parts in the denominator. The first part $\frac{1}{(n-1)^2}\frac{1}{x} + \frac{n^2}{(n-1)^2}\frac{1}{1-x}$ depends only on n, but the second part a depends also on ε_1 and ε_2, and as the second member of the inequality which is to be investigated, does depend only on n, we cannot expect the circumstance whether $\frac{d^2\psi}{dx_2} = 0$, when disappearing, lies in the positive region of $\frac{d^2\psi}{dv^2}$ or in the negative one, only to depend on the ratio of the size of the molecules. But this we may at once consider as a result obtained that as the parallel line is farther from the origin, and so the values of ε_1 and ε_2 are larger, the value of the first member of the inequality becomes smaller, and so there is a greater chance that the second member exceeds the first. For greater values of ε_1 and ε_2 there is a greater chance that the disappearance of $\frac{d^2\psi}{dx^2} = 0$ takes place in the region where $\frac{d^2\psi}{dv^2} < 0$, and the degree of the non-miscibility will be limited. Or rather, a phenomenon that attends non-miscibility, will be checked by this. Thus for $n = \infty$, for which $x = \frac{1}{3}$, and $y = \frac{1}{2}$, and $\frac{n}{n-1} = 1$, the first member of the inequality will be equal to 2 for the origin, to $\frac{2}{3}$ for the points of the tangent mentioned, and $\frac{1}{2}$ for the point P if we include also the lefthand part above the tangent in our calculation; the second member is equal to $\frac{2}{3}$. Then $\frac{d^2\psi}{dx^2} = 0$ disappears just on the verge of the region of $\frac{d^2\psi}{dv^2}$ positive or negative for the points of the tangent. For the points above the tangent, however, $\frac{d^2\psi}{dv^2} = 0$ disappears where $\frac{d^2\psi}{dv^2}$ is negative, and the reverse for the points below the tangent.

But let us try to answer the question where $\frac{d^2\psi}{dx^2} = 0$ disappears for arbitrary value of n. The relation between n, x, and y (Contribution III) is, indeed, a very intricate one — but to my astonishment it proved to be possible to find an answer by a comparatively simple reduction. If we start from equation (4) of Contribution III, we may write:

$$\frac{1}{n-1} + x = \frac{x(1-x)}{1-2x}\{1-y\}$$

and

$$\frac{n}{n-1} - (1-x) = \frac{x(1-x)}{1-2x}\{1-y\}$$

If we take the square of the first of these equations, and then divide by x — and the square of the second of these equations and then divide by $1-x$, the sum of the two values obtained yields:

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

For the second member may also be written $\frac{1}{4}\frac{(1-y)^2}{y^3}$, and the condition whether $\frac{d^2\psi}{dv^2}$ is positive or negative for the point in which $\frac{d^2\psi}{dx^2} = 0$ disappears, becomes then for the points below the tangent:

$$\frac{1}{1-\alpha+\frac{1}{4}\frac{(1-y)^2}{y^3}} \gtrless \frac{4y^2}{1+y}$$

In this equation we have $\alpha = 1$ for the origin and $\alpha = 0$ for the tangent itself. With $\alpha = 1$ we find as condition:

$$y(1+y) \gtrless (1-y)^2$$

For $y = \frac{1}{2}$, which belongs to $n = \infty$, the first member of the inequality is $\frac{3}{4}$, and the second member $\frac{1}{4}$. So, as we found above,

$\frac{d^2\psi}{dv^2} > 0$. But for $y = 0$, which would belong to $n = 1$, the first member $= 0$ and the second $= 1$. So for this limiting case $\frac{d^2\psi}{dv^2} < 0$. So there is a transition value of n, namely for that which belongs to $3y = 1$ or $y = \frac{1}{3}$. According to Contribution III the value of x is about 0.41 and of n about 3.4 for this value of y.

For the points of the tangent for which $\alpha = 0$, the condition is:

$$\frac{1}{1 + \frac{1}{4}\frac{(1-y)^2}{y^3}} \gtrless \frac{4y^2}{1+y}$$

or

$$0 \gtrless 4y^3 - 3y + 1$$

or

$$0 \gtrless (1 - 2y)^2 (1 + y).$$

So this inequality can never be satisfied by the sign $>$; only for $y = \frac{1}{2}$ there is equality, as we saw already above. We conclude from this that however great the value of n be, $\frac{d^2\psi}{dx^2} = 0$ disappears in the region where $\frac{d^2\psi}{dv^2}$ is negative for all the points of the tangents. So this is a fortiori the case for all the points above the tangent. When y lies between $\frac{1}{3}$ and $\frac{1}{2}$, and so $n > 3.4$, a line is to be indicated parallel to the tangent on which the points $(\varepsilon_1, \varepsilon_2)$ must lie for $\frac{d^2\psi}{dx^2} = 0$ to disappear, just on the verge of $\frac{d^2\psi}{dv^2} = 0$. But for values of $y < \frac{1}{3}$ and $n < 3.4$ the disappearance will take place where $\frac{d^2\psi}{dv^2}$ is negative for all the points below the parabola, and so the curve $\frac{d^2\psi}{dv_2} = 0$ will lie inside the curve $\frac{d^2\psi}{dv^2} = 0$ both at a temperature below T_1, so before the first contact, and at a temperature above T_2, so after the second contact. The place of the straight line which contains the points at which the transition of the sign of

$\frac{d^2\psi}{dv^2}$ takes place is determined by the value of $\alpha = 1 - \frac{3y-1}{4y^3}$ or $\alpha = \frac{(2y-1)^2(1+y)}{4y^3}$. So the quantity α has always the same sign, and as it cannot be greater than 1, y must always be greater than $\frac{1}{3}$. So the equation of this line is:

$$\frac{\varepsilon_1}{(n-1)^2}\frac{1}{x} + \frac{n^2\varepsilon_2}{(n-1)^2}\frac{1}{1-x} = \frac{3y-1}{4y^3}$$

Now we have also the means to decide whether the temperature at which $\frac{d^2\psi}{dx^2} = 0$ disappears, is higher or lower than the critical temperature of the mixture of the value of $x = x_g$ — in other words whether $T_g \gtrless T_k$. If $T_g < T_k$, then $\frac{d^2\psi}{dx^2} = 0$ has left the region where $\frac{d^2\psi}{dv^2} < 0$ on the side of the branch of the small volumes of $\frac{d^2\psi}{dv^2} = 0$, and this branch is still found even at the temperature T_g. For the other case we have a representation of the relative position of the two curves after they had left each other in fig. 10, Contribution III. The condition $T_g \gtrless T_k$ (see Contribution III) may be written:

$$\frac{2c}{b}x(1-x)\frac{1-y}{(1+y)^2} \gtrless \frac{8}{27}\frac{a}{b}$$

or

$$\frac{27}{4}\frac{cx(1-x)}{a} \gtrless \frac{(1+y)^2}{(1-y)}.$$

If we write further $\frac{cx(1-x)}{a} = \frac{1}{1-\alpha+\frac{(1-y)^2}{4y^3}}$, the condition becomes:

$$\frac{27}{4}\frac{1}{1-\alpha+\frac{(1-y)^2}{4y^3}} \gtrless \frac{(1+y)^2}{1-y}$$

For $\alpha = 1$, or for the origin O, this condition becomes:

$$27\,y^3 \gtrless (1+y)^2(1-y).$$

For $y = \frac{1}{2}$ or $n = \infty$ the first member of the inequality becomes equal to $\frac{27}{8}$, and the second member to $\frac{9}{8}$; which means that

$T_g = 3T_k$. But for $y = 0$ or $n = 1$ the first member $= 0$, and the second $= 1$. So there is a value of y, for which $T_g = T_k$, and of course this value must be larger than that which we found above, when we determined for what value of y the curve $\frac{d^2\psi}{dx^2}$ disappears on the boundary of $\frac{d^2\psi}{dv^2} = 0$. So if we put $y = \frac{1}{3}$ the first member is equal to 1, and the second to $\frac{32}{27}$. The equality of the two members requires y about 0,36, to which $n = 3.7$ corresponds, which is but little greater than we found above for the smallest value of n for which $\frac{d^2\psi}{dx^2} = 0$ goes beyond $\frac{d^2\psi}{dv^2} = 0$.

For the tangent for which $\alpha = 0$, the condition becomes:

$$\frac{27}{4} \frac{1}{1 + \frac{(1-4)^2}{4y^3}} \gtrless \frac{(1+y)^2}{(1-y)}$$

We cannot expect another value for the points of the tangent than $y = \frac{1}{2}$. The last inequality may also be written:

$$0 \gtrless (1-2y)^2 (1 + 4y + 10y^2 + y^3).$$

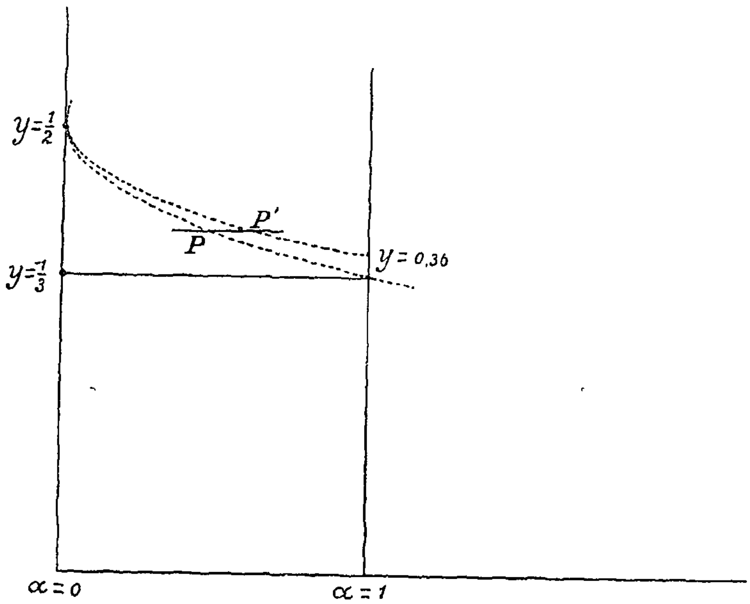

Fig. 38

If we call the value of α required to change the inequality into equality for given value of y, α' — then the relation:

$$1-\alpha'=\frac{27}{4}\frac{1-y}{(1+y)^2}-\frac{(1-y)^2}{4y^3},$$

holds for this quantity.

For the preceding problem, viz. the determination of the relation between α and y causing $\frac{d^2\psi}{dx^2}=0$ to disappear on the curve $\frac{d^2\psi}{dv^2}=0$,

$$1-\alpha=\frac{3y-1}{4y^3}$$

held.

For $\alpha'-\alpha$ we find then:

$$\alpha'-\alpha=\frac{1+y}{4y^2}-\frac{27}{4}\frac{1-y}{(1+y)^2}$$

or

$$\alpha'-\alpha=\frac{(1+y)^3-27\,y^2\,(1-y)}{4y^2\,(1+y)^2}=\frac{(1-2y)^2\,(1+7y)}{4y^2\,(1+y)^2}.$$

From this it appears, what had been clear beforehand, that α' is always greater than α, except for $y=\frac{1}{2}$, when they are both equal to 0, and so for the points of the tangent. A case, however, which we can only think as a limiting case, because it would require $n=\infty$. The adjoined figure 38 gives the relation between α and y for the two problems graphically. For the origin $\alpha=1$, and for the points of the tangent $\alpha=0$. For the first problem $y=\frac{1}{3}$ for the origin, and for the second $y=0{,}36$ — whereas for $\alpha=0$ the two values of y are $=\frac{1}{2}$. For the second problem the line $y=f(\alpha)$ always lies above that of the first problem. Hence for equal value of y the point P' lies at higher value of α than the point P.

(To be continued).