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Physics. — *"Contribution to the theory of binary mixtures"* XX. By Prof. J. D. VAN DER WAALS.

In the preceding Contribution I repeatedly pointed out that not all mathematical possibilities for partial miscibility really occur. Among others the case of only partial miscibility seems to be mathematically possible for all values of n and l, whereas for small value of n this partial miscibility has only been seldom observed. So if we want to find decisive rules for the occurrence of incomplete miscibility, this seems not possible to me without first having found a rule for the determination of the quantity l in the formula $a_{12}{}^2 = l a_1 a_2$. And this will no doubt require that we have first succeeded in forming a clear idea of what the cause is of the attraction of the molecules, so also of the cause which determines its value for a simple substance. But though the knowledge of the properties of the different mathematical possibilities, also in connection with the temperature, is not sufficient — and not even the principal factor that should be studied, still this knowledge is indispensable. And therefore I will start with giving some results about this.

In the formula:

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

the projection on the v,x-plane has been given of the section of the two curves $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ at the different temperatures, though on simplified suppositions. Of course there might also be given two such projections of this section on the v,T-plane and on the x,T-plane, which would also be closed curves. But the formulae for them would not be simple, and so we shall not try to give them. In both there would occur a minimum and a maximum of T, the minimum and the maximum value of v or of x being the same which also occur in the v,x-projection. If we imagine the three axes, an x-axis, a v-axis, and a T-axis, there is a closed curve in the space — and then the differential equation of this curve is given by a relation between dv, dx, and dT, which is derived from the simultaneously existing relation between these three differentials for the two functions $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$. These two relations are:

$$\frac{d^3\psi}{dT\,dv^2} dT + \frac{d^3\psi}{dv^3} dv + \frac{d^3\psi}{dx\,dv^2} dx = 0$$

and

$$\frac{d^3\psi}{dTdx^2}dT+\frac{d^3\psi}{dv\,dx^2}dv+\frac{d^3\psi}{dx^3}dx=0$$

If we take into account that $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^2\psi}{dx^2}=0$ for the points of this section, we may also write:

$$-\frac{2a}{v^3}\frac{dT}{T}+\frac{d^2p}{dv^2}dv+\frac{d^2p}{dx\,dv}dx=0$$

$$+\frac{2c}{v}\frac{dT}{T}-\frac{d^2p}{dx^2}dv+\frac{d^3\psi}{dx^3}dx=0.$$

We find for the relation between dT, dv, and dx then:

$$\frac{\frac{dT}{T}}{\begin{vmatrix}\frac{d^2p}{dv^2} & \frac{d^2p}{dx\,dv}\\ -\frac{d^2p}{dx^2} & \frac{d^3\psi}{dx^3}\end{vmatrix}}=\frac{dv}{\begin{vmatrix}\frac{d^2p}{dx\,dv} & -\frac{2a}{v^3}\\ \frac{d^3\psi}{dx^3} & \frac{2c}{v}\end{vmatrix}}=\frac{dx}{\begin{vmatrix}-\frac{2a}{v^3} & \frac{d^2p}{dv^2}\\ \frac{2c}{v} & -\frac{d^2p}{dx^2}\end{vmatrix}}$$

or

$$\frac{\frac{dT}{T}}{\frac{d^2p}{dv^2}\frac{d^3\psi}{dx^3}+\frac{d^2p}{dx\,dv}\frac{d^2p}{dx^2}}=\frac{dv}{\frac{2a}{v^3}\frac{d^3\psi}{dx^3}+\frac{2a}{v}\frac{d^2p}{dx\,dv}}=\frac{dx}{\frac{2a}{v^3}\frac{d^2p}{dx^2}-2\frac{c}{v}\frac{d^2p}{dv^2}}\ldots (1)$$

If the denominator of $\frac{dT}{T}$ is equal to 0, then T is either minimum or maximum; if the denominator dv is equal to 0, then v is either maximum or minimum, and if the denominator of dx is equal to 0, this holds for the limiting values of x.

We may also write the denominator of $\frac{dT}{T}$ thus:

$$\frac{d^2p}{dv^2}\frac{d^2p}{dx^2}\left[\left(\frac{dv}{dx}\right)'_T-\left(\frac{dv}{dx}\right)_T\right];$$

indicating by $\left(\frac{dv}{dx}\right)'_T$ the tangent of the angle which the tangent to the curve $\frac{d^2\psi}{dx^2}=0$ makes with the x-axis, and by $\left(\frac{dv}{dx}\right)_T$ the same quantity for the curve $-\frac{dp}{dv}=0$. For T minimum or maximum these curves touch, and also the locus of the points of intersection touches in that point. If at the minimum value of T we draw the three said curves in the v,x-projections, $\frac{d^2\psi}{dv^2}=0$ lies in the neighbourhood of the point of contact little above $v-b$, and with a curvature $\frac{d^2p}{dv^2}$ positive. The second curve $\frac{d^2\psi}{dx^2}=0$, also with a slight positive curvature, but yet somewhat more pronounced than the former curve, and finally the locus of the points of intersection, again with a somewhat intenser positive curvature. But at the maximum value of T the relative position of the three said curves is another, and there are even different possibilities.

First of all the relative position of $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^2\psi}{dx^2}=0$ may have remained the same, just as the sign of the curvature, and there may only be a difference in the position of the locus of the points of intersection, which has then the same point of contact as the two said curves, but lies on the other side of the tangent. Secondly the curvature of $\frac{d^2\psi}{dx^2}=0$ can be of inverse sign in the point of contact compared with that of $\frac{d^2\psi}{dv^2}=0$, and have the same sign as that of the locus of the points of intersection. Then $\frac{d^2\psi}{dx^2}=0$ must be quite contained within this locus at the moment of contact, and for higher T the curve $\frac{d^2\psi}{dx^2}=0$ must disappear in the region in which $\frac{d^2\psi}{dv^2}$ is positive, while in the former case this happens in the region where $\frac{d^2\psi}{dv^2}$ is negative.

This latter remark holds both if the second component, viz. that with molecules of greater size, has a higher T_k, and when T_{k_2} should be smaller than T_{k_1}, as for the system water-ether. But in all cases the value of the denominator of $\frac{dT}{T}$ in (1) begins with 0 at T_{min} and it ends with the same value at T_{max} If $\frac{d^2p}{dx^2}$ and $\frac{d^2p}{dv^2}$ could not become equal to 0, the difference of the value of $\left(\frac{dv}{dx}\right)_T$ for the two curves $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^2\psi}{dx^2}=0$ must begin with 0 for $T_{min.}$ and end with 0 for T_{max}. So on that side of the locus of the intersections where this difference is positive, there must be a maximum value for this difference, and on the side where this difference is positive, there must be a maximum value for this difference, and on the side where this difference is negative, a minimum value. Now this difference is positive on the side of the component with the greater size of the molecules and reversely. But also if it should be possible that $\frac{d^2p}{dv^2}$ and $\frac{d^2p}{dx^2}$ should be able to become equal to 0, the same remark holds for the denominator of $\frac{dT}{T}$, viz. that this denominator is always positive on the righthand side between $T_{min.}$ and T_{max} and reversely. But we shall yet have to return to the value of the denominator of $\frac{dT}{T}$, because the fact whether $\frac{d^2p}{dx^2}$ and $\frac{d^2p}{dv^2}$ can become equal to 0, is not entirely devoid of importance.

After this remark about the course of the value of the denominator of $\frac{dT}{T}$, we may als make a remark about the course of the value of the two other denominators in equation (1). First about the denominator of dx. If this denominator is equal to 0, x is either minimum or maximum. So if we examine the value of this denominator at the locus of the points of intersection, this value will begin with 0 and end again with 0 both on the lower and on the upper branch. On the upper branch it is negative, and on the lower branch it is positive. We can verify this by examining the sign of $T\frac{dv}{dT}$.

The denominator of dv is 0, when v has minimum or maximum value. Both on the righthand branch of the locus of the points of intersection of $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^3\psi}{dx^3}=0$ and on the lefthand branch the value of this denominator begins with 0 and ends with 0 at the minimum volume.

On the righthand side this value is always positive and reversely. We can verify this either by examining the sign of $T\frac{dv}{dT}$, or by examining the sign of $\frac{dv}{dx}$ for the locus of the points of intersection.

We shall now have to show that really from the value of the discussed denominators the above given sign of the value is to be derived. For this it is necessary to know the values of $\frac{d^2p}{dv^2}$, $\frac{d^2p}{dx\,dv}$, $\frac{d^2p}{dx^2}$, and $\frac{d^3\psi}{dx^3}$, bearing in mind that we have to do with points for which $\frac{d^2\psi}{dv^2}=0$.

For these values [1]) we find the following equations:

$$\left.\begin{aligned}
\frac{d^2p}{dv^2} &= \frac{2a}{v^4}\,\frac{3\,b-v}{v-b} \\
\frac{d^2p}{dxdv} &= -\frac{4a}{v^3}\left\{\frac{\frac{db}{dx}}{v-b}-\frac{1}{2}\,\frac{\frac{da}{dv}}{a}\right\} \\
\frac{d^2p}{dx^2} &= \frac{4a}{v^2}\left\{\frac{\left(\frac{db}{dx}\right)^2}{v(v-b)}-\frac{c}{2a}\right\} \\
\frac{d^3\psi}{dx^3} &= \frac{2a}{v^3}(v-b)^2\left\{\frac{2\left(\frac{db}{dx}\right)^3}{(v-b)^3}-\frac{1-2x}{x^2(1-x)^2}\right\}^{1)}
\end{aligned}\right\}\quad \ldots\ldots (2)$$

With introduction of these values the denominator of $\frac{dT}{T}$ has the complicated form:

$$\frac{4a^2}{v^4(v-b)}\left\{-6\left(\frac{\frac{db}{dx}}{v}\right)^3+2\frac{\frac{da}{dx}}{a}\left(\frac{\frac{db}{dx}}{v}\right)^2+2\frac{c}{a}\left(\frac{\frac{db}{dx}}{v}\right)- \right.$$
$$\left. -\frac{c\frac{da}{dx}}{a^2}\,\frac{v-b}{v}-\frac{3b-v}{v}\left(\frac{v-b}{v}\right)^2\frac{1-2x}{x^2(1-x)^2}\right\}$$

And the condition that the denominator of $\frac{dT}{T}$ be equal to 0, may be written as a third power equation in v, which in connection with the second power equation in v which holds for the intersection of $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^2\psi}{dx^2}=0$, can yield a relation in x for the determina-

[1]) These values were already used in Contribution XVIII, p. 888, where however the factor 2 has been omitted, which must be put for $\frac{\left(\frac{db}{dx}\right)^3}{(v-b)^3}$. On account of this here is an error in the equation following there.

tion of the points where this denominator is 0. This relation in x, however, has such an intricate form as to render it useless. We shall, however, return to this denominator later on.

The denominator of dx is equal to 0, when $\frac{a}{v^2}\frac{d^2p}{dx^2}=c\frac{d^2p}{dv^2}$. Now $\frac{d^2p}{dv^2}$ is positive, so long as $v<3b$. And though it is not impossible that for limiting values for x the circumstance $v=3b$, or even $v>3b$ can occur, this is among the very exceptional cases. As for the limiting values of x the value of $\frac{v}{b}$ is $=\frac{1}{1-x(1-x)\frac{c}{a}}$, the value of $x(1-x)\ \frac{c}{a}$ must be $>\frac{2}{3}$ for $v>3b$. For the present we shall not assume this case, but suppose $\frac{d^2p}{dv^2}$ positive for the limiting values of x.

Then it follows immediately from this that also $\frac{d^2p}{dx^2}$ is positive for the limiting values of x. From the given values for $\frac{d^2p}{dv^2}$ and $\frac{d^2p}{dx^2}$ follows:

$$\frac{4a^2}{v^4}\left\{\frac{\left(\frac{db}{dx}\right)^2}{v(v-b)}-\frac{c}{2a}\right\}=c\frac{2a}{v^4}\frac{3b-v}{v-b}$$

or

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

or

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

or

$$\left(\frac{db}{dx}\right)^2=\frac{c}{a}bv.$$

And if we substitute this value of $\left(\frac{db}{dx}\right)^2$ in the equation of the curve for the intersections, we find back:

$$v = \frac{b}{1-x(1-x)\frac{c}{a}}.$$

That we were justified in calling the case that $\frac{d^2p}{dv^2} \gtreqless 0$ for the limiting values very exceptional, may appear in the following way.

Let us write:

$$\frac{a}{cx(1-x)} = \frac{a_1}{c}\frac{1-x}{x} + \frac{a_2}{c}\frac{x}{1-x} + \left(\frac{a_1}{c} + \frac{a_2}{c} - 1\right)$$

or

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

or

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

For the limiting values of x:

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

And so we have for these values of x:

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

For limiting values of x near 0 or 1 this value would be very large. For the system water-ether we find with $n = 5\frac{1}{2}$ and x about 0.36 a value about equal to 2.3 and for $x = 0.98$ a very large value — so that the inverse value is by no means greater than $\frac{2}{3}$. If one of the limiting values of x happened to be equal to *the value of x, for which* $\frac{1}{x} + \frac{n^2}{1-x}$ *has the minimum value*, then $\frac{a}{cx(1-x)}$ would be equal to $\left(\frac{n+1}{n-1}\right)^2$, and if this value is to be smaller than $\frac{3}{2}$, n would have to be greater than 10 for the accidental case of the coincidence of the two said values of x.

The denominator of dv is positive so long as $\left(\frac{db}{dx}\right)^2$ is greater than $\frac{c}{a}bv$. If we put this condition in the equation of the curve of intersection, we find:

$$\frac{v}{b} < \frac{1}{1-x(1-x)\frac{c}{a}}$$

So the denominator of dx is positive throughout the lower branch of the curve of intersection, and inversely, as we had predicted above from the value of $T\frac{dx}{dT}$. But on the other hand this also shows that we have rightly made the denominator of $\frac{dT}{T}$ reverse its sign in the point where $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^2\psi}{dx^2}=0$ touch.

The denominator of dv is equal to 0 when $\frac{a}{v^2}\frac{d^3\psi}{dx^3}=-c\frac{d^2p}{dxdv}$. After some reduction of this relation if we introduce the above given value of $\frac{d^3\psi}{dx^3}$ and $-\frac{d^2p}{dxdv}$, we get of course the same equation as is yielded by differentiating $\frac{(v-b)^2}{x(1-x)}+\left(\frac{db}{dx}\right)^2=\frac{c}{a}v^2$ with respect to x, and putting the form obtained in this way equal to 0. I fully discussed the equation, which we then get, in Contribution XI (1908) and accordingly refer to this Contribution with an addition, however, which is not devoid of importance. It refers to the discussion about the obtained equation:

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

In this equation (These Proc. Vol. XI p. 429) the sign $+$ must be used in the numerator, when the value of $v<b_2$, and reversely. I have now come to see that this may also mean that the sign $+$ holds in the numerator for the determination of the minimum value of v, whereas the sign $-$ must be taken in the numerator for the determination of the maximum value of v.

For the determination of the value of x for the minimum volume the preceding equation may also be reduced to the form:

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

or $(n-1)\frac{a}{cx(1-x)}=n\sqrt{\frac{a_2}{c(1-x)^2}-1}+\sqrt{\frac{a_1}{cx^2}-1}$, while the sign between the two radical signs has to be replaced by — for the maximum volume.

By way of control I have calculated the different quantities in this formula for a system that cannot differ much from the system water-ether, and in this way computed the two values of $\frac{v}{b_1}$ corresponding to every value of x. For the limiting values of $x = 0,3$ and $0,97$ we compute from $x_1 x_2 = \frac{\varepsilon_1}{(n-1)^2}$ and from $(1-x_1)(1-x_2) = \frac{n^2\varepsilon_2}{(n-1)^2}$, for $n = \frac{11}{2}$ the value of $\varepsilon_1 = 5,893$ and $\varepsilon_2 = 0,0141$ and $n^2\,\varepsilon_2 = 0,426$.

Then the value of $\frac{a}{cx\,(1-x)} = \frac{1+\varepsilon_1}{(n-1)^2}\frac{1}{x} + \frac{n^2(1+\varepsilon_2)}{(n-1)^2}\frac{1}{1-x} - 1$ is:

x	$\frac{a}{cx\,(1-x)}$
0,3	2,294
0,4	2,374
0,5	2,709
0,6	3,352
0,7	4,533
0,8	7,021
0,9	14,517

From the equation:

$$\left(\frac{v}{b_1}\right)^2\left[1-x\;1-x)\frac{c}{a}\right] - 2\left(\frac{v}{b_1}\right)[1+\overline{n-1}\,x] + [1+(n^2-1)\,x] = 0$$

we find then for the following values of x the subjoined values of $\frac{v}{b_1}$ and $\frac{b}{b_1}$:

x	$\frac{v}{b_1}$	$\frac{b}{b_1}$
0,3	4,46	2,35
0,4	7 and 3	2,8
0,5	7,6 and 3,4	3,25
0,6	6,4 and 4,2	3,7

We see from this table that the minimum volume will occur for x about equal to 0,4, while the maximum volume occurs at x about 0,5. If we now also calculate $\sqrt{\frac{a_2}{c(1-x)^2} - 1}$ and $\sqrt{\frac{a_1}{cx^2} - 1}$, we find:

x	$\sqrt{\frac{a_2}{c(1-x)^2}-1}$	$\sqrt{\frac{a_1}{cx^2}-1}$
0,3	1,465	1,67
0,4	1,8006	1,0625
0,5	2,238	0,5981
0,6	2,923	*imaginary*

If to the n-fold of a value of the second column we add a corresponding value from the third column, and if we divide the sum by $n-1$, we find beginning with $x = 0,3$, successively the values 2,162, 2,437, and 2,87. From this we should conclude that the minimum value of v lies just before $x = 0,4$. With the sign — we find successively 1,42, 1,9645, and 2,602; and so the maximum volume at x somewhat above 0,5.

But to conclude from this example that the maximum volume is always greater than b_2, and the minimum volume always smaller, would be just as rash as my conclusion in Contribution XI that both maximum volume and minimum volume would always be smaller than b_2. Probably the case may occur that they are both smaller than b_2, and possibly also that they are both even greater than b_2.

If they are both smaller than b_2, the equation:

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

must be satisfied for two values of x, for both with the sign $+$; and if they could both be greater than b_2, then also if the sign between the two terms of the second member has been replaced by —. To examine what conditions the binary systems must satisfy for one of these three cases to take place, we should examine the properties of the 3 functions which occur in this equation.

The first function $\frac{a}{cx(1-x)}$ is infinitely great for $x = 0$ and $x = 1$, and has a smallest value for certain value of x. From the form:

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

follows for the value of x at which the minimum occurs:

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

or $x = 0,325$. The minimum value itself is equal to:

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

and is calculated from it equal to 2,265. Those numerical values, of course, only hold for the system water-ether. So in the little table on p. 1225 the first value still refers to the descending branch. The first term of the second member, viz. $\sqrt{\frac{a_2}{c(1-x)^2}}-1$, begins at $x=0$ with the value $\sqrt{\frac{n^2(1+\varepsilon_2)}{(n-1)^2}}-1$, and ends at $x=1$ with an infinite value. It is ascending throughout, and nowhere imaginary; the third quantity, viz. $\sqrt{\frac{a^1}{cx^2}}-1=\sqrt{\frac{1+\varepsilon_1}{(n-1)^2\,x^2}}-1$, becomes equal to 0 for $x=\sqrt{\frac{1+\varepsilon_1}{(n-2)^2}}$, if $\frac{1+\varepsilon_1}{(n-1)^2}<1$. It begins infinitely great, is descending throughout, and becomes, as we shall suppose, equal to 0; in that point its differential quotient is infinite.

If we write the equation which is to be satisfied, in the following form:

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

$$=\frac{n}{(x-1)}\frac{1}{\sqrt{(1-x)}}\sqrt{\frac{a_2}{c(1-x)}-(1-x)}\pm\frac{1}{(n-1)}\frac{1}{\sqrt{x}}\sqrt{\frac{a_1}{cx}-x}$$

we can to decide which of the three cases about the value of maximum or minimum volume is to be expected, in the first place propose the question whether the first member is greater or smaller than the second member for the value of x, which makes the third term equal to 0.

For this value of x the first member is equal to $\frac{a_2}{c}\frac{1}{1-x}-(1-x)$ and the second member $\frac{n}{n-1}\sqrt{\frac{a_2}{c(1-x)}-(1-x)}$, and so we have to put the question whether

$$\sqrt{\left\{\frac{a_2}{c(1-x)}-(1-x\right\}}\gtrless\frac{n}{n-1}\frac{1}{v}(1-x)$$

or

$$\frac{c_2}{c}\frac{1}{1-x}-(1-x)\gtrless\frac{n^2}{(n-1)^2}\frac{1}{1-x}$$

or

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

or

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

or

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

or

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

Now for the system water-ether the sign $<$ holds as ε_2 is so small, and this implies that for the mentioned value of x

$$\frac{a}{cx(1-x)} < \frac{n}{n-1} \sqrt{\frac{a_2}{c(1-x)^r} - 1}.$$

If this result is represented graphically, as has been done in fig. 53, the point P of the curve B lies within the curve A, and the ordinates of B must be both augmented and diminished by an amount indicated by the third curve C, to intersect the curve A. Then the point where the curve B itself intersects A must lie at a value of x between that for which the volume is minimum or maximum; and this is quite in accordance with our former results for the system under consideration. And always when the point P lies within A, or when $n\sqrt{\varepsilon_2} < (n-1) - \sqrt{1+\varepsilon_1}$, the maximum volume will be greater than b_2, and the minimum volume smaller than b_2.

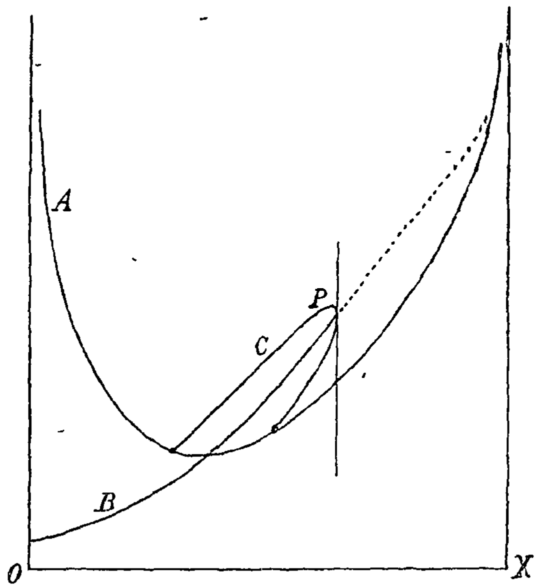

Fig. 53.

But there are other cases possible for which:

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

and then the result is different. Then the point P lies outside the curve A. First of all we might think, that B had not yet intersected the curve A before the point P, and then intersection with A can only be brought about by increase of the ordinates of B by a certain amount in which case two points of intersection appear. Then both maximum and minimum volume are smaller than b_2, and this case I had considered as the only possible one in Contribution XI. We might possibly also think that the point P lies below A, but that B had first intersected this curve twice, and then we might even ask whether intersection with A might not be brought about both by increase of the ordinates of B and by diminution with those of C. Then we should get 4 points of intersection. But then the extreme values of x would have to be rejected as lying outside the locus of the sections of $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^2\psi}{dx^2}=0$. That I think a closer investigation necessary for this apparently unimportant matter is owing to my desire to get more certainty about the mixtures of hydrocarbons and alcohols. Are systems conceivable for them which account for the phenomena without it being necessary for us to attribute them to an unknown abnormality of the alcohols? Would perhaps the case $v > b_2$ occur for them for both volumes?

So

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

for the systems for which the two terms in the second member of the equation are connected by the same sign for maximum and minimum volume, and also $n\sqrt{\varepsilon_2} < (n-1) - \sqrt{\varepsilon_2}$ must hold. And so there must be a perceptible difference between ε_1 and $1+\varepsilon_1$ or ε_1 not much greater than 1, as for water-ether. It must be rather smaller than 1; and ε_2 must not be small, as for water-ether. If we lower the parabola of fig. 36 in the direction of the ε_1-axis with unity, the point $\varepsilon_1, \varepsilon_2$ must lie within the new parabola, but it must remain below the original one. Only for values of n which are greater than 2 does this new condition diminish the place for the choice of the points $\varepsilon_1, \varepsilon_2$. But if we put $n < 2$, the equation which we have used to determine the value of x for the point P, could no longer be satisfied. This value, equal to $\frac{\sqrt{(1+\varepsilon_2)}}{n-1}$, would then be greater than 1, and then no such point could be indicated between $x=0$ and $x=1$. But this is a drawback only in appearance. Nothing compels us to restrict the discussion about the equation:

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

to values of x lying between 0 and 1. Only if we should find $x>1$ we should have to reject a point for which $x>1$ as irrelevant to our question. But if the use of $x>1$ should be objected to, we might confine our consideration to values of $x<1$, but so near 1, that the value of $\frac{1}{1-x}$ far exceeds all other terms. It then appears that the value of the first member, in any case in which ε_2 is positive, far exceeds the value of the first term of the second member. Then the two values under consideration are:

$$\frac{a_2}{c(1-x)} \text{ and } \frac{n}{n-1}\sqrt{\frac{a_2}{c(1-x)^2}}.$$

If the two quantities are divided by the same factors, it appears that so long as $1+\varepsilon_2$ is >1, the curve A lies above the curve B.

Also in a simpler way we might arrive at the result that if:

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

both maximum volume and minimum volume lie on the same side of a straight line $v=b_2$.

If we write in

$$\frac{(v-b)^2}{x(1-x)} + (b_2-b_1)^2 = \frac{c}{a}v^2$$

the value b_2 for v, and seek the values of x, for which this then holds, we get the equation

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

So the value of $v=b_2$ is not possible if

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

According to our above remark this condition is satisfied for $n \leqslant 2$. Most probably this means then that all the values of v are smaller than b_2. Then the case that all the values are greater than b_2, could not occur for n small, then the abnormality of alcohol would consist in this that it behaves as if it consisted of very great molecules.

Accordingly I have not yet succeeded in finding a system for which the curve B intersects the curve A twice in such a way that also the phenomena of unmixing if n is not great, are accounted for. For the present, however, I shall go on with the subject treated in this and in the preceding contribution.

Chemistry. — "*The nitration of ortho-chlortoluene*". By Prof. A. F. HOLLEMAN and Dr. J. P. WIBAUT.

(This communication will not be published in these Proceedings).

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