Chemistry. — *"Equilibria in systems, in which phases, separated by a semi-permeable membrane."* XIV. — By F. A. H. SCHREINEMAKERS.

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Deduction of some properties of isotonic curves in ternary systems, in which dimixtion into two liquids occurs.

In order to deduce and to elucidate further the properties, discussed in the previous communication we contemplate fig. 1 in which $f_1\ q_1\ h_1$ and $f_2\ q_2\ h_2$ represent a part of the binodalcurve. The isotonic W-curve going through the two conjugated points is represented by the dotted curve $a\,b\,q_1\ \ c\,d\,q_2\,e$. We are able to represent the composition, the thermodynamical potential, etc. of an arbitrary phase Q, which contains the components $W\ X$ and Y, not only with the aid of the quantities of those three components, but also with the aid of three arbitrary other phases (provided that they are not situated on a straight line); previously we have called those phases "composants" in distinction with the components, of which this phase Q consists [1]).

As many properties can be deduced more easily with the aid of composants than of components, we now shall use those composants.

We choose as composants 1. the diffusing substance W, 2. an arbitrary liquid b, 3. an arbitrary phase F. As we have seen formerly (l. c.) we can represent the composition of an arbitrary liquid p by:

$$m \text{ quantities of } W + n \text{ quantities of } F + (1-m-n) \text{ quantities of } b \quad (1)$$

so that we call b as fundamental composant. Consequently we have in fig. 1 a system of coordinates with the point b as origin and the lines $b\,W$ and $b\,F$ as axes. If we draw in the figure the lines $p\,p_1$ and $p\,p_2$ parallel to $b\,W$ and $b\,F$ then is (l. c.)

$$m = \frac{pp_1}{bW} \qquad n = \frac{pp_2}{bF} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

If we take for m as unity of length bW and for n as unity of length bF then we can put:

$$m = pp_1 \qquad n = pp_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

In order to represent the composition of a liquid with the aid of com-

[1]) For a contemplation more in detail of components and composants comp.: In-, mono- and plurivariant equilibria. Comm. XXIV and XXV.

ponents in the communications XXIV and XXV we have used always x and y as variables, but, if we used composants, always m and n. As, however, now we do not compare both methods with one another and therefore no confusion can occur, we shall take for the composants also x and y as variables.

Consequently we represent the composition of an arbitrary liquid p by:

x quant. of $W + y$ quant. of $F + (1-x-y)$ quant. of b, (4)

so that in fig. 1 bW represents the X-axis and bF the Y-axis. Therefore we have in the figure:

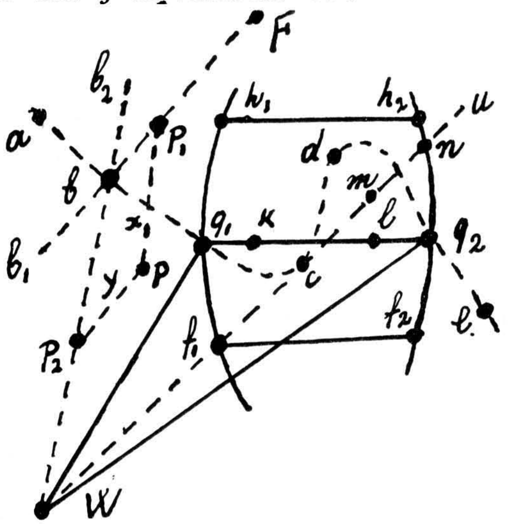

Fig. 1.

$$x = pp_1 \qquad y = pp_2.$$

If we put in (4) $x=0$ and $y=0$ then p coincides with point b; for $y=0$ p is situated anywhere on the line bW; for $y=0$ and $x=1$ p coincides with point W. If $x+y=1$ then p is situated anywhere on the line WF. If we give a negative value to x or y or $1-x-y$, then p falls outside the composants-triangle bWF.

We now take a liquid L with the composition as in (4) and a liquid L_1 with the composition:

$$x_1 \text{ quant. of } W + y_1 \text{ quant. of } F + (1-x_1-y_1) \text{ quant. of } b$$

and we now consider the osmotic equilibrium:

$$L \mid L_1 \quad \ldots \ldots \ldots \quad (5)$$

in which the substance W only diffuses through the membrane. We assume that there are n quantities of L and n_1 quantities of L_1. If δn quantities of W (water) diffuse from L towards L_1, then x and y change with:

$$dx = \frac{nx-\delta n}{n-\delta n} - x = -\frac{(1-x) \, . \, \delta n}{n-\delta n}$$

$$dy = \frac{ny}{n-\delta n} - y = \frac{y \, . \, \delta n}{n-\delta n} \quad \ldots \ldots \quad (6)$$

while x_1 and y_1 change with:

$$dx_1 = \frac{(1-x_1) \, \delta n}{n_1+\delta n} \qquad dy_1 = -\frac{y_1 \, \delta n}{n_1+\delta n} \quad : \ldots \ldots \quad (7)$$

The total thermodynamical potential of the osmotic system (5) now changes with:

$$(n-\delta n)\left(\zeta+\frac{\partial\zeta}{\partial x}dx+\frac{\partial\zeta}{\partial y}dy\right)+(n+\delta n)\left(\zeta_1+\frac{\partial\zeta_1}{\partial x_1}dx_1+\frac{\partial\zeta_1}{\partial y_1}dy_1\right)- \\ -n\zeta-n_1\zeta_1 \quad . \quad (8)$$

in which ζ and ζ_1 represent the thermodynamical potentials of the liquids L and L_1. With the aid of (6) and (7), (8) passes into:

$$\left[\zeta_1+(1-x_1)\frac{\partial\zeta_1}{\partial x_1}-y_1\frac{\partial\zeta_1}{\partial y_1}-\zeta-(1-x)\frac{\partial\zeta}{\partial x}+y\frac{\partial\zeta}{\partial y}\right]\delta n \quad . \quad . \quad (9)$$

As the thermodynamical potential of a system in equilibrium is not allowed to change, (9) must be zero for infinitely small positive and negative values of ∂n. Consequently the osmotic system (5) is in equilibrium if:

$$\zeta+(1-x)\frac{\partial\zeta}{\partial x}-y\frac{\partial\zeta}{\partial y}=\left[\zeta+(1-x)\frac{\partial\zeta}{\partial x}-y\frac{\partial\zeta}{\partial y}\right]_1 , \quad . \quad . \quad . \quad (10)$$

The $O. W. A.$ (osmotic water attraction) of an arbitrary liquid is defined therefore by:

$$\varphi=\zeta+(1-x)\frac{\partial\zeta}{\partial x}-y\frac{\partial\zeta}{\partial y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Previously (Comm. II) we have found, using components for the $O. W. A.$

$$\varphi=\zeta-x\frac{\partial\zeta}{\partial x}-y\frac{\partial\zeta}{\partial y};$$

the origin of the system of coordinates was situated then in point W and now in the point b.

We now replace the liquid L_1 of equilibrium (5) by the liquid b of fig. 1; we then have the osmotic equilibrium:

$$L \mid L_b \text{ (fig. 1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

As x_1 and y_1 for liquid b are zero, it follows from (10) that the liquid L is defined by:

$$\zeta+(1-x)\frac{\partial\zeta}{\partial x}-y\frac{\partial\zeta}{\partial y}=\left[\zeta+\frac{\partial\zeta}{\partial x}\right]_b \quad . \quad . \quad . \quad . \quad . \quad (13)$$

which represents the equation of the isotonic curve going through point b. From (13) follows:

$$[(1-x)\,r-ys]\,dx+[(1-x)\,s-yt]\,dy=0 \quad . \quad . \quad . \quad . \quad (14)$$

in which:

$$r=\frac{\partial^2\zeta}{\partial x^2} \quad s=\frac{\partial^2\zeta}{\partial x\partial y} \quad t=\frac{\partial^2\zeta}{\partial y^2}.$$

If we take the liquid L of equilibrium (12) in the vicinity of the point b (fig. 1) then x and y approach zero, r s and t rest finite, if b represents a ternary liquid. (14) now passes into:

$$r\,dx + s\,dy = 0 \qquad \frac{dy}{dx} = -\frac{r}{s} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

by which the direction of the isotonic curve in point b is defined. Of course this relation is valid for every arbitrary point of an isotonic curve, f. i. for the points a, q, c, d, q_2, e etc. but not for its terminating-points on the sides of the components-triangle.

As is known from the theory of the ternary liquids, outside the region of dimixtion is:

$$r > 0 \qquad t > 0 \qquad rt - s^2 > 0 \quad . \quad . \quad . \quad . \quad . \quad (16)$$

This is also the case on the binodalcurve itself. Within the region of dimixtion however a curve (not drawn in the figure) proceeds, on which:

$$rt - s^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

This is the spinodalcurve, which is situated within the binodalcurve, but touches this in the critical points. Within this spinodalcurve is:

$$rt - s^2 < 0$$

and also may be $r \gtreqless o$ and $t \gtreqless o$. Is one of the magnitudes r or t negative, then $r\,t—s^2$ is negative also; of course the reverse is not the case.

If k and l in fig. 1 represent the points of intersection of the spinodalcurve with the line $q_1\,q_2$, then $r\,t—s^2$ is zero in those points, therefore; between q_1 and k and q_2 and l it is positive and between k and l negative.

The direction of the isotonic curve is defined by (15) in the point b; as b is situated outside the region of dimixtion, r is $>$ o, but the sign of s is indefinite. If s is negative, then it follows from (15) that the isotonic curve is situated in the vicinity of the point b within the angle $W\,b\,F$ (and its opposite angle $b_1\,b\,b_2$); if s is positive, then the curve is situated within the angles $b_1\,b\,W$ and $b_2\,b\,F$. If $s = o$ then the curve touches in point b the Y-axis viz. the line $b\,F$. As r is never zero in the point b, the curve can, therefore, never touch the X-axis viz. the line $b\,W$ in b.

Above we have seen already that (15) is true for every arbitrary point of an isotonic curve; as in every point outside the region of dimixtion r is > 0, none of the lines Wa, Wq_1, Wq_2 and We can touch this curve, therefore. Hence follows the property, already discussed before:

the part of an isotonic W-curve, situated *outside* a region of dimixtion has such a form that every straight line, going through point W, intersects this curve in one point only and never touches it.

We now consider the part $q_1\,c\,d\,q_2$ of the isotonic curve, situated within the region of dimixtion and we assume that r is zero in the points c and d and is negative, therefore, between c and d. It now follows from (15) that the isotonic curve touches the lines Wc and Wd in c and d. If we imagine within the angle cWd a straight line going through point W, then this intersects the isotonic curve in three points. Consequently we find:

the part of an isotonic W-curve, situated *within* a region of dimixtion *can* have such a form that we are able to draw from point W straight lines which touch this branch or intersect it in three points.

If r is positive in all points of the part of the isotonic curve, situated between q_1 and q_2, then for this part the same is true as for the part, which is situated outside the region of dimixtion. This is the case f. i. with the curves 4 and 6 of fig 1. (Comm. XIII).

In order to examine the binodal-curve in the vicinity of the points q_1 and q_2 we take as composants q_1 q_2 and W, we represent the composition of two arbitrary liquids L_1 and L_2 by:

x_1 quant. of $W + y_1$ quant. of $q_2 + (1-x_1-y_1)$ quant. of q_1

x_2 quant. of $W + y_2$ quant. of $q_2 + (1-x_2-y_2)$ quant. of q_1.

Consequently we take a system of coordinates with point q_1 as origin q_1 W as X-axis and $q_1 q_2$ as Y-axis. If L_1 and L_2 are two conjugated liquids, then the equilibrium $L_1 + L_2$ is defined by the three equations:

$$\left.\begin{aligned}\left(\zeta - x\frac{\partial\zeta}{\partial x} - y\frac{\partial\zeta}{\partial y}\right)_1 = \left(\zeta - x\frac{\partial\zeta}{\partial x} - y\frac{\partial\zeta}{\partial y}\right)_2 \\ \left(\frac{\partial\zeta}{\partial x}\right)_1 = \left(\frac{\partial\zeta}{\partial x}\right)_2 \qquad \left(\frac{\partial\zeta}{\partial y}\right)_1 = \left(\frac{\partial\zeta}{\partial y}\right)_2\end{aligned}\right\} \quad . \quad . \quad , \quad (18)$$

We find those equations by expressing that the total thermodynamical potential of the equilibrium $L_1 + L_2$ does not change, if small quantities of each of the three components q_1 q_2 and W pass from the one liquid into the other. It follows from (18):

$$(xr + ys)_1\, dx_1 + (xs + yt)_1\, dy_1 = (xr + ys)_2\, dx_2 + (xs + yt)_2\, dy_2 \quad (19)$$

$$r_1\, dx_1 + s_1\, dy_1 = r_2\, dx_2 + s_2\, dy_2 \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$s_1\, dx_1 + t_1\, dy_1 = s_2\, dx_2 + t_2\, dy_2 \quad . \quad . \quad . \quad . \quad . \quad (21)$$

We now let coincide the liquids L_1 and L_2 with the points q_1 and q_2; therefore we have to put:

$$x_1 = 0 \qquad y_1 = 0 \qquad x_2 = 0 \qquad y_2 = 1 \quad . \quad . \quad . \quad . \quad (22)$$

If we substitute those values in equations (19) and if we neglect the terms of higher order than the first, we find:

$$0 = s_2\, dx_2 + t_2\, dy_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

The binodal-curve in the vicinity of the points q_1 and q_2 is defined, therefore, by (20), (21) and (23). Instead of (21) we now may write also:

$$s_1\, dx_1 + t_1\, dy_1 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

If we substitute in (20) the values of dy_1 and dy_2 which follow from (24) and (23) then we find:

$$\frac{r_1 t_1 - s_1^2}{t_1} dx_1 = \frac{r_2 t_2 - s_2^2}{t_2} dx_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Hence is apparent that dx_1 and dx_2 have always the same sign. This means: if a liquid is situated on $q_1 h_1$ $(q_1 f_1)$ then the conjugated liquid is situated on $q_2 h_2$ $(q_2 f_2)$.

Equation (24) defines the direction of the binodal curve in the point q_1; we have viz.:

$$\frac{dy_1}{dx_1} = -\frac{s_1}{t_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

The direction of the isotonic curve is defined in every point by (15), in the point q_1 therefore, we have to give to r and s in (15) the values r_1 and s_1. We then have:

$$\frac{dy}{dx} = -\frac{r_1}{s_1} \qquad \frac{dy_1}{dx_1} = -\frac{s_1}{t_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

the first of which defines the direction of the isotonic curve, the second defines the direction of the binodal curve in the point q_1. As r_1 and t_1 are positive, $r_1 : s_1$ and $s_1 ; t_1$ have always the same sign, therefore. If $s_1 = o$ then follows:

$$\frac{dy}{dx} = \infty \qquad \frac{dy_1}{dx_1} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

It now follows from (29) and (28):
the binodal curve and an isotonic curve are situated in the vicinity of their point of intersection either both within the conjugation-angle or both within the supplement-angle. If the binodal curve touches the one leg of the angle, then the isotonic curve touches the other leg.

The *O. W. A.* of an arbitrary liquid L is defined by (11). For a liquid in the vicinity of L is true, therefore:

$$d\varphi = [(1-x)\,r - y\,s]\,dx + [(1-x)\,s - y\,t]\,dy \quad . \quad . \quad . \quad (29)$$

If we take the liquid L in the point q_1 (fig. 1) and if we take again the same components as above, consequently q_1 as origin of the system of coordinates, then x and y become zero. (29) then passes into:

$$d\varphi = r_1\,dx + s_1\,dy \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

If we proceed from q_1 along the binodal curve towards a point in the immediate vicinity, then the relation (24) is true for dx and dy. Hence follows for (30):

$$d\varphi = \frac{r_1 t_1 - s_1^2}{t_1} . dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

in which the coefficient of dx is positive. We now proceed from q_1 in the direction towards h_1 or, as we have expressed it in the previous communication: we proceed starting from the point q_1 along the binodal curve away from point W. As then dx is negative, $d\varphi$, therefore, is also negative and consequently the $O. W. A.$ increases. Therefore we find:

the $O. W. A.$ of the liquids of a binodal curve increases in that direction in which we move away from the point W.

We have already applied this property in order to define the direction in which the $O. W. A.$ of the liquids increases along the binodal curve of the figs. 1—3 (previous Communication).

In the previous Communication we have discussed already, that the isotonic curve, which goes through m_1 (figs 2 and 3 Comm. XIII), touches the binodal curve in this point m_1. A second branch of the isotonic curve, which is situated, however, totally within the region of dimixtion, also touches the binodal curve in the point m_2.

In order to examine the isotonic curve and the binodal curve in the vicinity of those points, we take as composants: W m_1 and an arbitrary phase F. Consequently we take a system of coordinates with m_1 as origin, m_1 W as X-axis and m_1 F as Y-axis.

For the isotonic curve, going through point m_1, equation (15) is true, in which we have to give to r and s the values, which they have in m_1. If we take those r_1 and s_1, then curve 2 (fig. 2 XIII) and curve 5 (fig. 3 XIII) in the vicinity of m_1 are defined by:

$$\frac{dy}{dx} = -\frac{r_1}{s_1} \quad \ldots \ldots \ldots \quad (32)$$

For an equilibrium $L_1 + L_2$ the equations (18) are true and the equations (19)—(21) which follow from this. We now imagine the liquids L_1 and L_2 in the points m_1 and m_2, so that:

$$x_1 = 0 \quad y_1 = 0 \quad y_2 = 0 \quad \ldots \ldots \quad (33)$$

Limiting ourselves to terms of the first order, then (19)—(21) pass into:

$$0 = x_2 (r_2\, dx_2 + s_2\, dy_2)$$

$$r_1\, dx_1 + s_1\, dy_1 = r_2\, dx_2 + s_2\, dy_2$$

$$s_1\, dx_1 + t_1\, dy_1 = s_2\, dx_2 + t_2\, dy_2.$$

Hence follows:

$$r_1\, dx_1 + s_1\, dy_1 = 0 \quad \frac{dy_1}{dx_1} = -\frac{r_1}{s_1} \quad \ldots \ldots \quad (34)$$

by which the direction of the binodal curve in m_1 is defined. It is apparent from (32) and (34) that the isotonic curve and the binodal curve touch one another in m_1.

If we take as composant m_2 instead of m_1, then we have to exchange the indices 1 and 2 in the deduction above, hence follows that the isotonic curve and the binodal curve touch one another also in the point m_2 (figs. 2 and 3 XIII).

The change of the $O.W.A.$ of a liquid L is defined by (29); therefore is true for the liquid m_1 (fig. 2 and 3 XIII):

$$d\varphi = [(1-x_1)\,r_1 - y_1\,s_1]\,dx_1 + [(1-x_1)\,s_1 - y_1\,t_1]\,dy_1 \quad . \quad . \quad (35)$$

As however $x_1 = 0$ and $y_1 = 0$, (35) passes into:

$$d\varphi = r_1\,dx_1 + s_1\,dy_1 . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

We now choose the new liquid on the binodal curve so that dx_1 and dy_1 satisfy (34); then follows:

$$d\varphi = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

Hence follows the property, already formerly discussed:
the $O.W.A.$ of the liquids of a binodal curve is maximum or minimum in the points, which are situated on the conjugation-line going through W (figs. 2 and 3 XIII).

We have assumed in the deductions above that the points m_1 and m_2 represent ternary liquids, so that $m_1\,m_2$ is a ternary conjugation-line.

If, however, m_1 and m_2 are binary liquids, then the deductions are valuable no more. If we imagine the line $Wm_1\,m_2$ (figs. 2 and 3 XIII) coinciding with one of the sides of the components-triangle, then t_1 and t_2 are infinitely large, but $y_1\,t_1$ and $y_2\,t_2$ rest finite for $y_1 = 0$ and $y_2 = 0$. It now follows from (19) — (21):

$$\left.\begin{aligned} y_1\,t_1\,dy_1 &= x_2\,(r_2\,dx_2 + s_2\,dy_2) \\ r_1\,dx_1 + s_1\,dy_1 &= r_2\,dx_2 + s_2\,dy_2 \\ t_1\,dy_1 &= t_2\,dy_2 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (38)$$

while (14) which defines the direction of the isotonic curve, passes into:

$$r_1\,dx + (s_1 - y_1\,t_1)\,dy = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

From (38) follows for the binodal curve

$$r_1\,dx_1 + \left(s_1 - \frac{y_1\,t_1}{x_2}\right)dy_1 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

It is apparent from (39) and (40) that the isotonic curve and the binodal curve do not touch one another now, a property to which we have pointed in the previous communication.

Above we have seen that the $O.W.A.$ of the liquids of the binodal curve in the points m_1 and m_2 (figs. 2 en 3 XIII) is a maximum or minimum; we now shall consider this case more in detail.

We have represented the compositions of the liquids with the aid of the composants Wm_1 and F, in which F is an arbitrary phase. We now choose F in such a way that s_1 becomes $= 0$. (Later on it will appear that F is situated then anywhere on the tangent going through point m_1). If we involve in (19) — (21) also terms of higher order and if we put:

$$x_1 = 0 \quad y_1 = 0 \quad y_2 = 0 \quad s_1 = 0 \quad . \quad . \quad . \quad . \quad . \quad (41)$$

then we get:

$$\frac{1}{2} r_1 \, dx_1^2 + \frac{1}{2} t_1 \, dy_1^2 = x_2 (r_2 \, dx_2 + s_2 \, dy_2) + A_2 \quad . \quad . \quad . \quad (42)$$

$$r_1 \, dx_1 + \frac{1}{2} \frac{\partial s_1}{\partial y_1} dy_1^2 = r_2 \, dx_2 + s_2 \, dy_2 + B_2 \quad . \quad . \quad . \quad . \quad (43)$$

$$t_1 \, dy_1 + C_1 = s_2 \, dx_2 + t_2 \, dy_2 + C_2 \quad . \quad . \quad . \quad . \quad . \quad (44)$$

In the first part of (43) the terms with $dx_1 \, dy_1$ and dx_1^2, which are infinitely small with respect to dx_1, are omitted. A, B and C contain the terms of the second order. We can satisfy those equations by taking dy_1 dx_2 and dy_2 of the same order and dx_1 of the order dy_1^2, while $r_2 \, dx_2 + s_2 \, dy_2$ is also of the order dy_1^2. Consequently we may write for (42)—(44):

$$\frac{1}{2} t_1 \, dy_1^2 = x_2 (r_2 \, dx_2 + s_2 \, dy_2) + A_2 \quad . \quad . \quad . \quad . \quad . \quad (45)$$

$$r_1 \, dx_1 + \frac{1}{2} \frac{\partial s_1}{\partial y_1} dy_1^2 = r_2 \, dx_2 + s_2 \, dy_2 + B_2 \quad . \quad . \quad . \quad . \quad (46)$$

$$t_1 \, dy_1 = s_2 \, dx_2 + t_2 \, dy_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

Herein is:

$$A_2 = \frac{1}{2}\left(r + x \frac{\partial r}{\partial x}\right)_2 dx_2^2 + \left(s + x \frac{\partial r}{\partial y}\right)_2 dx_2 \, dy_2 + \frac{1}{2}\left(t + x \frac{\partial s}{\partial y}\right) dy_2^2 \quad (48)$$

$$B_2 = \frac{1}{2} \frac{\partial r_2}{\partial x_2} dx_2^2 + \frac{\partial r_2}{\partial y_2} dx_2 \, dy_2 + \frac{1}{2} \frac{\partial s_2}{\partial y_2} dy_2^2 \quad . \quad . \quad . \quad . \quad (49)$$

It follows from (45) and (46):

$$r_1 \, dx_1 + \frac{1}{2}\left(\frac{\partial s_1}{\partial y_1} - \frac{t_1}{x_1}\right) dy_1^2 = -\frac{1}{x_2}\left(\frac{1}{2} r \, dx^2 + s \, dx \, dy + t \, dy^2\right)_2 . \quad (50)$$

It follows from (46) and (47):

$$t_1 \, s_2 \, dy_1 = - D \, dx_2 \quad t_1 \, r_2 \, dy_1 = D \, dy_2 . \quad . \quad . \quad . \quad . \quad (51)$$

in which:

$$D = r_2 \, t_2 - s_2^2 .$$

The terms of higher order are neglected in (51); if we substitute the values of dx_2 and dy_2 from (51) in the second part of (50), then we find:

$$r_1 \, dx_1 + \frac{1}{2}\left(\frac{\partial s_1}{\partial y_1} - \frac{t_1}{x_2} + \frac{t_1^2 \, r_2}{x_2 D}\right) dy_1^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad (52)$$

by which the binodal curve is defined in the vicinity of the point m_1.

In a similar way we find from (14) for the isotonic curve:

$$r_1 \, dx + \frac{1}{2}\left(\frac{\partial s_1}{\partial y_1} - t_1\right) dy^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

and for the change of the $O. W. A.$ from (35):

$$d\varphi = r_1\, dx_1 + \frac{1}{2}\left(\frac{\partial s_1}{\partial y_1} - t_1\right) dy_1^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

We now choose dx_1 and dy_1 in such a way that the new liquid is situated on the binodal curve; consequently dx_1 and dy_1 must satisfy (52); then we may replace (54) by:

$$d\varphi = \frac{1}{2}\left(1 - x_2 - \frac{t_1\, r_2}{D}\right)\frac{t_1}{x_2} \cdot dy_1^2. \quad . \quad . \quad . \quad . \quad . \quad (55)$$

Instead of by (37) $d\varphi$ is defined, therefore, by a magnitude of the second order. With the aid of (51) we are able to give still another form to (55), viz.:

$$d\varphi = \frac{1}{2}\left(1 - x_2 - \frac{dy_2}{dy_1}\right)\frac{t_1}{x_2} \cdot dy_1^2 \, . \quad . \quad . \quad . \quad . \quad (56)$$

It follows from (52) and (53) that the binodal curve and the isotonic curve are parabolic in the vicinity of m_1 and touch both the Y-axis in m_1. In order to define the position of those curves with respect to one another, we imagine in the figures to be drawn a line $m_1' W_1'$, parallel to and in the vicinity of $m_1 W$. For the point of intersection of $m_1' W_1'$ with those curves then is valid $dy = dy_1$. It follows then from (52) and (53):

$$\left(\frac{\partial s_1}{\partial y_1} - t_1\right) dx_1 = \left(\frac{\partial s_1}{\partial y_1} - \frac{t_1}{x_2} + \frac{t_1 r_2}{x_2 D}\right) dx \quad . \quad . \quad . \quad . \quad (57)$$

If we put:

$$\frac{\partial s_1}{\partial y_1} - t_1 = -\, Q_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

then we may write (57) with the aid of (55):

$$dx_1 - dx = 2\,\frac{d\varphi}{dy_1^2} \cdot \frac{dx}{Q_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

If we consider the value of Q_1 from (58), then follows from (53) that dx and Q_1 have the same sign, so that $dx : Q_1$ is always positive; the sign of (59) is the same, therefore, as that of $d\varphi$.

In order to apply the above equations, we shall distinguish different cases:

A. Binodal curve and isotonic curve in m_1; fig. 2 XIII.

The origin of the system of coordinates is situated, therefore, in point m_1 of the figure. If we imagine the conjugation-line $a_1\, a_2$ in the vicinity of $m_1\, m_2$, then we find:

$$\frac{a_1\, m_1}{W m_1} > \frac{a_2\, m_2}{W m_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

As $a_1\, m_1 = d\, y_1$, $a_2\, m_2 = d\, y_2$, $W\, m_1 = 1$ and $W\, m_2 = 1 - x_2$ in which x is negative, therefore, we may write for (60), if we take positive dy_1 and dy_2, also

$$dy_1 > \frac{dy_2}{1-x_2} \quad \ldots \ldots \ldots \ldots \quad (61)$$

or:

$$1 - x_2 - \frac{dy_2}{dy_1} > 0 \quad \ldots \ldots \ldots \ldots \quad (62)$$

If we take dy_1 and dy_2 both negative, then we find also (62).

As x_2 is negative, it follows from (56):

$$d\varphi < 0 \quad \ldots \ldots \ldots \ldots \quad (63)$$

Consequently φ is a maximum in m_1; the *O. W. A.* is a minimum in m_1, therefore. This is in accordance with the direction of the arrows on the binodal curve (fig. 2 XIII). It now follows from (59) in connection with (63):

$$dx_1 < dx \quad \ldots \ldots \ldots \ldots \quad (64)$$

This means: if we proceed along the line $m_1'W_1'$ (see above) in the direction towards the point W, then we meet firstly the binodal curve and afterwards the isotonic curve; we see that this is in accordance with the figure.

B. Binodal curve and isotonic curve in m_1; fig. 3 XIII.

The origin of the system of coordinates is situated, therefore, in point m_1 of the figure; x_2 is positive now. In the same way as in A we find again (62); as, however, x_2 is positive, it now follows:

$$d\varphi > 0 \quad \ldots \ldots \ldots \ldots \quad (65)$$

In accordance with the direction of the arrows in the figure, it follows, therefore, that the *O. W. A.* in m_1 is a maximum. In connection with (65) it follows from (59):

$$dx_1 > dx \quad \ldots \ldots \ldots \ldots \quad (66)$$

This is in accordance with the position of the binodal curve and the isotonic curve in the vicinity of point m_1.

In order to consider the curves in the vicinity of the point m_2, we may use also the equations (52)—(59); then, however, we have to replace the index 1 by 2 and x_2 by x_1. We call those new equations (52^a)—(59^a); with the aid of (60) we find instead of (62):

$$1 - x_1 - \frac{dy_1}{dy_2} < 0 \quad \ldots \ldots \ldots \ldots \quad (67)$$

We now distinguish two cases.

C. Binodal curve and isotonic curve in m_2; fig. 2 XIII.

The origin of the system of coordinates is situated now in the point m_2 of the figure; x_1 is positive but smaller than 1. With the aid of (67) we find from (56ª) that $d\varphi < 0$, which is in accordance with (63), as is necessary.

Instead of (64) we find from (59ª):

$$dx_2 < dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (68)$$

This is in accordance with the position of the two curves in the vicinity of point m_2; the branch of the isotonic curve which touches the binodal curve in m_2 is situated viz. within the region of dimixtion.

D. Binodal curve and isotonic curve in m_2; fig. 3 XIII.

The origin of the system of coordinates is situated now in the point m_2 of the figure; x_1 is negative. With the aid of (67) we now find from (56ª) that $d\varphi > 0$. This is in accordance with (65). Instead of (66) now is:

$$dx_2 > dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (69)$$

This is also in accordance with the figure; the branch of the isotonic curve, which touches the binodal curve in m_2, is situated viz. within he region of dimixtion.

(*To be continued*).